hexane followed by $CHCl_3$ containing increasing concns of MeOH. The hexane–$CHCl_3$ (2:3, 1:4) and $CHCl_3$ eluate fractions were rechromatographed through a silica gel column eluting with petrol containing increasing concns of $CHCl_3$ in petrol followed by $CHCl_3$ containing increasing concns of MeOH in $CHCl_3$. Compound **2** (2 mg) was obtained from the petrol–$CHCl_3$ (3:2) eluate after recrystallization from EtOAc; mp 245°; IR ν_{max}^{KBr} cm^{-1}: 3400, 1745, 1730, 1700, 1604, 1300, 1220, 1130, 1080; UV λ_{max}^{EtOH} nm (poorly soluble): 237, 260 (sh), 297; ^1H NMR ($CDCl_3$): δ 10.54 (1H, *s*, CHO), 7.92 (1H, *s*, exch. D_2O), 6.75 (1H, *s*), 6.49 (1H, *s*, Ar–H), 4.01 (2H, *q*, $J = 7.0$ Hz), 3.98 (3H, *s*, OMe), 2.57 (3H, *s*, Ar–Me), 2.30 (3H, *s*, Ar–Me), 1.29 (3H, *t*, $J = 7.0$ Hz); ^{13}C NMR ($CDCl_3$): see Table 1. MS: *m/z* (%, rel. int.): 416 $[M+2]^+$ (3), 415 $[M+1]^+$ (25), 414 $[M]^+$ (95), 370 (11), 369 (42), 368 (100), 341 (15), 340 (30), 312 (16), 287 (16), 285 (11), 210 (19), 191 (11), 58 (33), 43 (56). Accurate mass measurement: found: 414.0952; $C_{21}H_{18}O_9$ requires 414.0949.

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PHENYL INDANE FROM *ACORUS CALAMUS*

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Key Word Index—*Acorus calamus*; Araceae; rhizomes; *Z*-3-(2,4,5-trimethoxy phenyl)-2-propenal; 2,3-dihydro-4,5,7-trimethoxy-1-ethyl-2-methyl-3-(2,4,5-trimethoxyphenyl)indene.

Abstract—Besides three known compounds, two new compounds, namely *Z*-3-(2,4,5-trimethoxy phenyl)-2-propenal and a new phenyl indane have been isolated from the rhizomes of *Acorus calamus*. These compounds have been characterized from their spectral data and by synthesis.

INTRODUCTION

Asarone, the principal constituent of the essential oil of *Acorus calamus* is well known as an insect growth regulator [1]. Since asarone is not entirely responsible for the physiological activity shown by *A. calamus* oil, it was thought worthwhile to reexamine the oil.

RESULTS AND DISCUSSION

The rhizomes of *A. calamus* were dried and then exhaustively extracted with ethanol. The solvent was evaporated and the resulting extract was subjected to rigorous CC over silica gel to give five compounds. Three of these compounds were identified as *Z*-3-(2,4,5-trimethoxy phenyl)-1-propene (asarone, a liquid), 2,4,5-trimethoxybenzaldehyde, mp 115° (lit. [2], mp 115°) and acoradin (a dimer, mp 99°, lit. [2] mp 101°) from their spectral data and comparison with the literature [2]. Besides the known compounds two more compounds were isolated, **4** and **5**.

Compound **4**, $C_{12}H_{14}O_4$, $[M]^+$ 222, mp 85°, was obtained as a colourless crystalline compound from acetone in the form of needles. It gave a positive test with 2,4-DNP indicating the presence of a carbonyl function. The IR spectrum showed strong absorption at 1650 cm^{-1}

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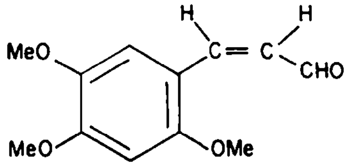
*Contribution No. 273.



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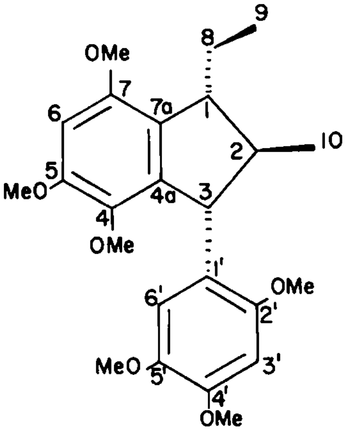

5

and a weak doublet at 2830 cm^{-1} for a conjugated CHO. The ^{1}H NMR showed signals at δ10.7 (CHO), a multiplet at 6.50 and a doublet at 6.80 (J = 6.0 Hz) due to the *cis*-configuration of an α,β-unsaturated aldehyde together with signals for three methoxyls. Compound **4** thus was characterised as *Z*-3-(2,4,5-trimethoxyphenyl)-2-propenal, which was further supported by its synthesis from the selenium dioxide oxidation of pure asarone. The spectral data were identical.

Compound **5**, $C_{24}H_{32}O_6$, $[M]^+$ 416.2214, mp 84°, an amorphous substance, could not be crystallized. The ^{1}H NMR spectrum of this compound integrated for six methoxyls indicating it to be a possible dimer of asarone like acoradin, a symmetrical cyclobutane dimer already reported from this plant [2]. Like acoradin it is not a symmetrical dimer as the three singlets for the six methoxyl groups at δ3.40, 3.70 and 3.84 integrated for three, three and 12 protons, respectively. It was interesting to note from the ^{1}H NMR spectrum that the aromatic region integrated for three protons indicating that one proton of one of the rings participates in the dimerization. The other groups indicated were an ethyl group at δ0.87 (3H, *t*, J = 6.5 Hz, H-9), 1.63 (2H, *m*, H-8), 2.07 (1H, *m*, H-1), a secondary methyl group (1.20, 3H, *d*, J = 6.5 Hz, H-10), 2.73 (1H, *m*, H-2) and a proton on a carbon atom attached to the phenyl ring (4.37, 1H, *d*, J = 5.0 Hz, H-3). From the above data and taking into consideration its molecular formula, compound **5** was thought to be a tricyclic compound. Such tricyclic compounds have been prepared synthetically from propenphenyl ethers [3]. The above skeleton was further supported by ^{13}C NMR spectral data (Table 1) and mass spectral fragmentation pattern *m/z* (rel. int.): 416.22 $[M]^+$ (100), 387.17 $[M-Et]^+$ (3.8), 233.10 $[387-5\times OMe]$ (2.7), 219.07 $[233-Me]$ (90.1). On the basis of ^{1}H NMR, ^{13}C NMR and major fragments in the mass spectrum structure **5** is proposed.

The stereochemistry of **5** is in complete agreement with the proposed γ-racemates prepared by earlier workers [3] from isohomogenol and isosafrole. Finally, the structure was confirmed by synthesis from asarone by the method reported earlier [3]. Spectral data were comparable. This appears to be the first report on the occurrence of such a compound in nature. It is therefore identified as 2,3-dihydro-4,5,7-trimethoxy-1-ethyl-2-methyl-3-(2,4,5-trimethoxyphenyl) indene.

Table 1. ^{13}C NMR spectral data of compound **5**

C	δ (multiplicity)	C	δ (multiplicity)
1	47.94 (*d*)	1'	127.37 (*s*)
2	48.82 (*d*)	2'	148.05 (*s*)
3	52.64 (*d*)	3'	98.23 (*d*)
4,7	151.10 (*s*)	4'	139.59 (*s*)
5	139.59 (*s*)	5'	127.48 (*s*)
6	97.29 (*d*)	6'	113.27 (*d*)
4a,7a	152.28 (*s*)	6 × OMe	55.46 (*q*)
8	26.79 (*t*)		56.42 (*q*)
9	11.75 (*q*)		56.89 (*q*)
10	22.09 (*q*)		

EXPERIMENTAL

All mps are uncorr. IR spectra were recorded in KBr. ^{1}H NMR spectra were measured at 60 MHz using TMS as int. ref.; values are reported in δ units. MS were determined at 70 eV with an EI probe. ^{13}C NMR were run at 22.5 MHz in $CDCl_3$.

Isolation and purification. Plant material was collected at the vegetative stage of growth from the Jammu region at an altitude of *ca* 300 m during August, 1978. Identification of the plant was carried out at the Herbarium of RRL, Jammu. Air dried rhizomes of *A. calamus* L. were exhaustively extracted with 95% EtOH. The solvent was evapd *in vacuo* and the residue extracted with Na_2CO_3 soln. The insoluble portion was chromatographed on a silica gel column (180 x 2 cm) using petrol as eluent. The petrol eluate containing a number of compounds was further chromatographed over silica gel successively with hexane, C_6H_6, $CHCl_3$ and 5% MeOH in $CHCl_3$ to give five compounds. Three of these were identified as asarone, asaraldehyde and acoradin (mp, IR, NMR and MS). Characterization of other two compounds is based on the data given below.

Z-3(2,4,5-Trimethoxyphenyl)-2-propenal (**4**). Rigorous CC of C_6H_6 fractions on crystallization from Me_2CO gave fine, colourless needles, mp 85°. They gave a positive test with 2,4-DNP. IR ν_{max}^{KBr} cm^{-1}: 2830, 1650, 1495, 1460, 1270, 1205, 1155, 870, 820, 740, 660. ^{1}H NMR ($CDCl_3$): δ3.87, 3.90, 4.00 (9H, *sss*, 3 × OMe), 6.5, 7.3 (2H, *ss*, H-3 and H-6), 6.50 (1H, *m*, H-2α), 6.80 (1H, *d*, $J = 6.0$ Hz, H-3β), 10.70 (1H, *s*, CHO). MS *m/z* (rel. int.): 222.0 $[M]^+$ (50.47), 195 $[M - CO + H]^+$ (100), 191.0 (68.30), 152 (27.73), 137 (27.60), 122 (12.62). Found: C, 64.97; H, 6.28. $C_{12}H_{14}O_4$ requires: C, 64.86; H, 6.30.

2,3-Dihydro-4,5,7-trimethoxy-1-ethyl-2-methyl-3-(2,4,5-trimethoxyphenyl)indene (**5**). Fractions, eluted with 5% MeOH in $CHCl_3$, gave an amorphous powder which could not be crystallized, mp 84°. IR ν_{max}^{KBr} cm^{-1}: 1605, 1575, 1505, 1480, 1390, 1335, 1330, 1200, 1170, 1070, 1035, 975, 880, 800, 770. ^{1}H NMR ($CDCl_3$): 0.87 (3H, *t*, $J = 6.5$ Hz, H-9), 1.20 (3H, *d*, $J = 6.5$ Hz, H-10), 1.63 (2H, *m*, H-8), 2.07 (1H, *m*, H-1), 2.73 (1H, *m*, H-2), 3.40 (3H, *s*, OMe), 3.70 (3H, *s*, OMe), 3.84 (12H, *s*, 4 × OMe), 4.37 (1H, *d*, $J = 5.0$ Hz, H-3), 6.41 (2H, *d*, $J = 3.0$ Hz, H-3′ and H-6′), 6.57 (1H, *s*, H-6). MS *m/z* (rel. int.): 416.2214 $[M]^+$ (100), 387.1724 (3.8), 385.2059 (6.1), 356.0760 (3.0), 341.1260 (2.6), 247.1284 (2.8), 233.1044 (2.7), 220.0921 (13.6), 219.0781 (90.1), 217.0377 (2.8). Found: C, 69.40; H, 7.79. $C_{24}H_{32}O_6$ requires C, 69.23; H, 7.70.

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SURANGIN C, A COUMARIN FROM *MAMMEA LONGIFOLIA*

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Key Word Index—*Mammea longifolia*; Guttiferae; bark; 4-alkylated coumarins; surangin B; surangin C.

Abstract—The isolation and characterization of a new 4-alkylated coumarin is described.

INTRODUCTION

The roots of *Mammea longifolia* (Wight) Planch and Triana have been shown [1] to contain the coumarins surangin A (**1**) and B (**2**) and taraxerol. In the course of our search for the presence of new pesticides in Indian plants we have found that the bark of *M. longifolia* contains surangin B and its deacetyl analogue, which we have named surangin C (**3**). Unlike the roots, the bark contained neither surangin A nor taraxerol.

RESULTS AND DISCUSSION

Surangin C (**3**), $C_{27}H_{36}O_6$, gave a green colouration with methanolic ferric chloride. The presence of three hydroxyl functions was established by the formation of a triacetate derivative. Its IR and UV properties [$\nu_{max}^{CHCl_3}$ cm^{-1}: 3500–3100 (br), 1720, 1610, 1595, 1380 and 1200; UV λ_{max}^{MeOH} nm (log ε): 227 (4.01), 256 (4.75) and 333 (4.51)] showed it to be a coumarin closely related to surangins A and B [1]. Its ^{1}H NMR spectrum was very similar to that of surangin B with the exception that it lacked an acetate singlet at δ2.2 and a one proton multiplet at δ6.5. However, an additional one proton multiplet was present at δ4.68 which suggested that surangin C possibly contained a hydroxyl function at methylene b instead of the acetoxyl present in surangin B. This was confirmed from the ^{1}H NMR spectrum of surangin C triacetate in which the multiplet at δ4.68 was replaced by multiplet of the same magnitude at δ6.25. In order to establish the total structure, decoupling experiments at several sites in the ^{1}H NMR spectrum of

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