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0014-4754/83/090988-04$1.50 + 0.20/0

Short Communications

Ferric chloride oxidation of isoeugenol[1]

Y.H. Kuo and S.T. Lin

Department of Chemistry, National Taiwan University, Taipei (Taiwan), January 20, 1983

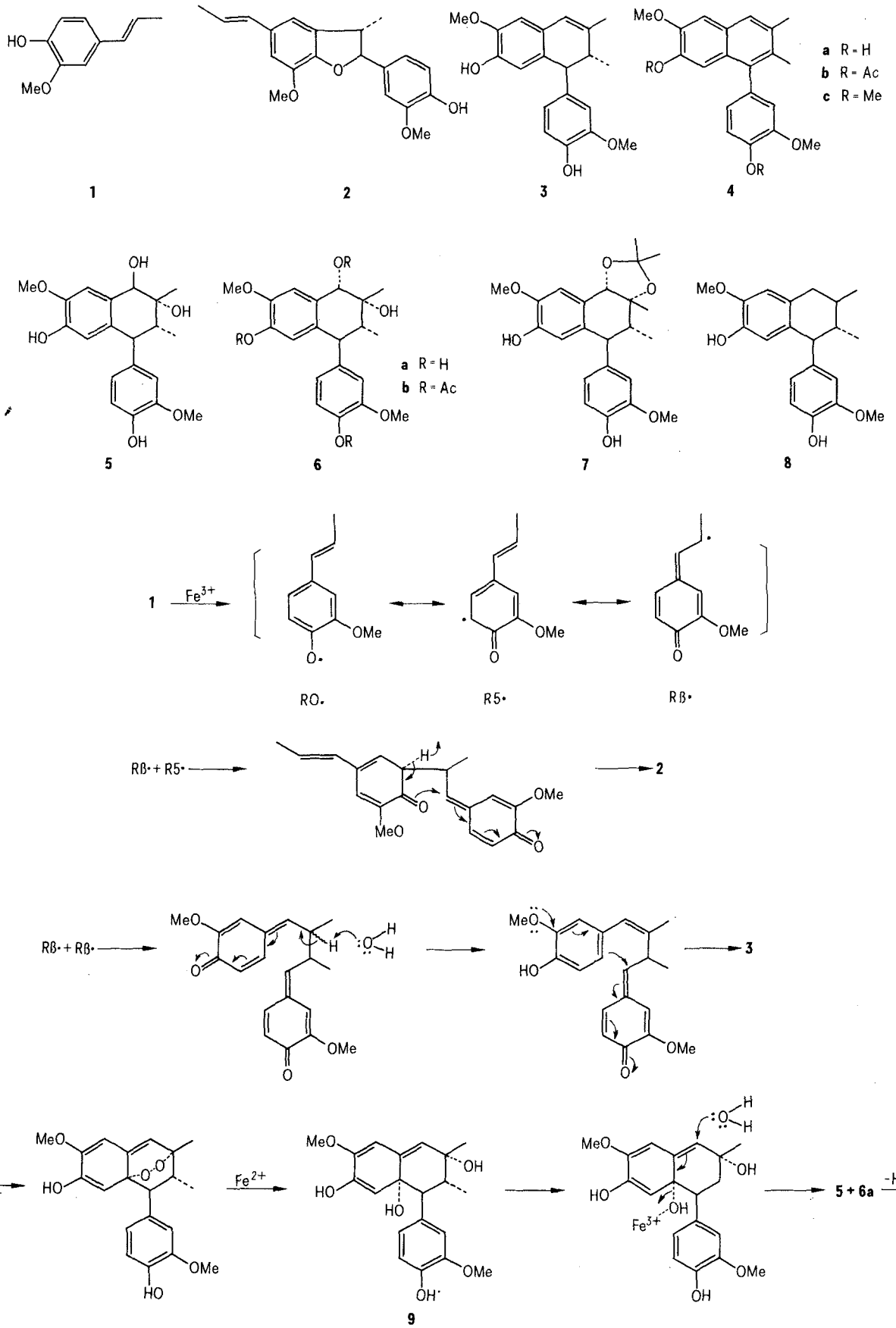
Summary. Ferric chloride oxidation of isoeugenol gave 5 products. The elucidation of the structures of those products and the mechanism of their formation are discussed.

Material and methods. The oxidation of isoeugenol **1** has been studied previously as a model for the observation of the formation of lignin-related dimers during ferric chloride oxidation[2] and enzymatic oxidation[3]. Photolysis[4] and free radical oxidation[5] of isoeugenol also give similar products. Further studies showed that free radical oxidation of isoeugenol[6] produced 4 trilignols. In all other experiments reported[7], the ferric chloride oxidation of isoeugenol yielded only product dehydrodiisoeugenol **2**. In the experiments described here, the oxidation of isoeugenol (10 g) acetone solution with aqueous ferric chloride in order to prepare **2** actually yielded 4 crystalline products, **3** (14 mg), **4a** (120 mg), **5** (16 mg) and **6a** (58 mg) in addition to **2** (5.3 g). The products are dilignols with a new C_β-C_β linkage except that **2** is dilignol with a C_α-O linkage. The structures were elucidated as follows.

Result and discussion. **4a** (m.p. 219–220 °C) shows IR-absorption bands at ν_{max} 3400, 1600 and 1500 cm^{-1} and NMR signals at δ_{CD_3OD} 2.11 and 2.42 (each 3H, s), 3.84 and 3.98 (each of 3H, s), 6.66, 6.70 and 7.00 (each 1H, ABX system), 7.04, 7.30 and 7.47 (each 1H, s). Its acetate **4b** (m.p. 176–177 °C), prepared from **4a** with Ac_2O-pyridine, expressed 2 acetyl groups [ν_{max} 1760 cm^{-1}; δ_{CDCl_3} 2.16 and 2.28 (each 3H, s)] instead of 2 hydroxy groups. With diazomethane the tetramethyl ether **4c** (m.p. 178–179 °C) was obtained. It was identical with dehydroguaiaretic acid dimethyl ether[8] isolated from *Guaiacum officinale.* **6a** (m.p. 247–249 °C) is a tetraol (ν_{max} 3485, 3420, and 3250 cm^{-1}) whose structure was elucidated by analytic and spectral data of its triacetate **6b**. **6b** (m.p. 216–218 °C) exhibits bands at 3520, 1760, 1715, 1605 and 1505 cm^{-1} in the IR and signals at δ_{CDCl_3} 0.93 (3H, d, J = 7Hz), 1.34 (3H, s), 1.92 (1H, s, −OH), 2.05–2.25 (1H, m, C(2)-H), 2.12, 2.21 and 2.31 (each 3H, s), 3.70 (1H, d, J = 9Hz, C(1)-H), 3.81 (6H, s), 5.87 (1H, s, C(4)-H), 6.65 and 7.11 (each 1H, s), and 6.83, 6.82 and 7.08 (each 1H, ABX system). **6a** gave **4a** on refluxing in acetone solution with p-TsOH. According to the spectral data, 2 hydroxyl groups must be located on C(3) and C(4). **6a** was not hydrogenolyzed with 10% Pd-C in methanol indicating that the C(1)-hydroxyl group has an α-equatorial orientation. The 1,2-glycol was shown to be cis because **6a** gave an amorphous acetonid **7** [ν_{max} 3400, 1580, 1110, and 1010; δ_{CDCl_3} 2.16 (6H, s)]. The large coupling constant (J = 9Hz) of C(1)-H indicates that both aryl and methyl groups have a diequatorial orientation.

5 (m.p. 210–211 °C) is also a tetraol (ν_{max} 3400 and 3225 cm^{-1}); its structure was elucidated by analytic and spectral data. **4a** was also obtained from **5** by treatment with acid. Both aryl group and methyl group in **5** have a diequatorial orientation due to C(1)-H with large coupling constant δ_{CD_3OD} 3.48 (1 H, d, J = 9 Hz). The C(4)-H signal appears at δ 4.19 (s). Therefore that 2 hydroxyl groups are located at C(3) and C(4) position. **5** gave no reaction with 2,2-dimethoxypropane in the presence of acid. The result indicates that the 1,2-glycol is a diaxial orientation. **3** (m.p. 158–159 °C, λ_{max} 281 nm; log 4.50) exhibits bands at 3390, 1600 and 1510 cm^{-1} in the IR and signals at δ_{CDCl_3} 1.06 (3H, d, J = 7Hz), 1.77 (3H, d, J = 1.2Hz), 2.36 (1H, m, C(2)-H), 3.63 (1H, d, J = 3Hz, C(1)-H), 3.78 and 3.80 (each 3H, s), 5.43 and 5.45 (each 1H, s, 2-OH), 6.09 (1H, br s, C(4)-H), and 6.50–6.80 (5H, m). Treatment with OsO_4 in pyridine yielded **6a**. The hydrogenation product of **3** was identical with quaiacin **8** (m.p. 197–199 °C).[9] In the tetrahydronaphthalene derivatives **5**, **6**, **7**, and **8** the aryl groups prefer to be in quasi-equatorial orientation. But in the dihydronaphthalene derivative (as **3**), the aryl group prefers the quasi-axial orientation. Therefore C(1)-H of **3** shows a small diequatorial coupling constant (J = 3Hz)[10].

Scheme


1
2
3
4
a R = H
b R = Ac
c R = Me
5
6
a R = H
b R = Ac
7
8
1 Fe3+
RO·
R5·
Rß·
Rß· + R5·
2
Rß· + Rß·
3
3O2
Fe3+
Fe2+
9
5 + 6a
-H2O
4

The reaction starts from a RO· radical which exhibits 2 other resonance hybride Rβ· and R5· radicals (see scheme). Coupling between Rβ· radical and R5· radical generates **2**[7d] and the combination of 2 Rβ· radicals yields **3**. **3** is oxidized with oxygen and $FeCl_3$ as catalyst[11] to the endoperoxide **9** which is reduced by Fe^{2+} ion and finally rearranged by $FeCl_3$ to give **5** and **6a**. **4a** is formed by dehyration of **5** and **6a** during the separation.

1 The study was supported by the National Science Council of ROC.

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0014-4754/83/090991-03$1.50 + 0.20/0

Ortho-aminoacetophenone: A component of the sex pheromone system of the web-spinning larch sawfly, *Cephalcia lariciphila* wachtl

R. Baker, C. Longhurst[1], D. Selwood and D. Billany

Chemical Entomology Unit, Departments of Biology and Chemistry, The University of Southampton, Southampton SO9 5NH (England), and Forestry Commission, Alice Holt Lodge, Wrecclesham, Farnham, Surrey GU10 4LH (England), January 5, 1983

Summary. The ortho-isomer of aminoacetophenone was found in females of *Cephalcia lariciphila*. The pheromone released antennal movement, abdominal flexing and short flights in males, but did not release orientated upwind flight in these activated males.

Males of *Cephalcia lariciphila* have been shown to respond to a sex pheromone produced by the female[2]. In an attempt to identify the pheromonal components of female *C. lariciphila* large scale collections of prepupae were made from the Forest of Dean (SO 650160) and Mortimer Forest (SO 625350) in February and March of 1979–1981.

Females were extracted into pentane using a procedure similar to that developed for *Diprion* spp.[3]. The insects were macerated in methanol and ultrasonicated. The mixture was then refluxed for 24 h; after centrifugation the supernatant methanol was refluxed with KOH. The methanol was then evaporated and following addition of water the residue was extracted with pentane. Volatile compounds in the pentane extract were resolved on a SCOT capillary GLC column (5% carbowax 20 M, 0.2 mm × 50 m; 130–200 °C at 4 °C/min) or a 2% OV17 on diatomite CLQ column (100–200 mesh, 3 mm × 3 m; 130–315 °C at 6 °C/min). Mass-spectra of the eluting compounds were recorded at 70 eV on an A.E.I. MS30 spectrometer with a Kratos DS55 data system. One of the major non-hydrocarbon peaks (< 0.5 µg/female) was identified as an isomer of aminoacetophenone, m/e (%), 136 (8), 135 (81), 121 (10), 120 (100), 93 (5), 92 (46), 65 (22), 39 (7). Comparison with authentic samples of *o*-, *p*- and *m*-aminoacetophenone (aap) confirmed the natural product to be the *ortho*-isomer. This compound has previously only been reported in the

Table 1. Responses of male *Cephalcia lariciphila* to virgin females, female extract and *o*-aminoacetophenone*

Behavioral response	Number of males giving the behavioral response (number tested)				
	Virgin female (10)	Female extract (12)	*o*-Amino aceto-phenone (15)	Solvent control (10)	Virgin male (10)
1. Antennal movement	10	12	15	0	4
2. Abdomenal flexing	10	12	15	0	1
3. Short flights (100 mm)	9	7	12	0	1
4. Upwind flight	6	4	0	0	0
5. Courtship	3	0	0	0	0

* Assay chamber of same basic design as Jones et al.[6] but with a 1.1 m diameter × 2 m chamber and without hexagonal interface to give a laminar airflow. Males released from 200 × 200 mm platform 0.5 m above the chamber floor and upwind of the female. Females and test substances were placed on a 100 × 100 mm platform at the other end of the chamber. Females were placed in 40 × 35 mm high perforated plastic chambers.

Table 2. Response of male *C. lariciphila* to delta and horizontal board traps baited with isomers of aminoacetophenone, female extracts or virgin females

	Trap type	Mean number of males/trap		
		Experiment 1	Experiment 2	Experiment 3
o-Aminoacetophenone	Delta		3.2b	4.4c
	Board	36.0b		29.6b
m-Aminoacetophenone	Delta		0.8b	
	Board	5.6c		
p-Aminoacetophenone	Delta		2.4b	
	Board	10.2c		
Female extract (0.5 equivalent)	Delta		27.8a	
	Board	42.4b		
Virgin female	Delta			96.6a
	Board	94.2a		
Control	Delta		1.4b	3.4c
	Board			10.2c

Mean trap catches followed by the same letter in any experiment are not significantly different at $p > 0.05$; ANOVA followed by Newman Keul's test. Experiment 1 performed in 1980, experiment 2 in the period 7.–12.5.81 and experiment 3 in the period 12.–19.5.81.