tic set of parameters for these interactions render this analysis suspect. We expect from the method of preparation and the overall chemistry (i.e. the known product being sulphited in the 2 position)[7] the anion **3**. For this, except for the protons of the methyl group, none are symmetrically equivalent and 6 different hyperfine splittings might be present ($a_{CH_3} \neq a_3 \neq a_5 \neq a_6 \neq a_7 \neq a_8$). Presupposing **1** anion structure and interpreting the spectrum on the basis of an accidental equivalence of protons 5, 6, 7, 8, provides the excellent fit shown in the stick diagram (Figure 1). The hyperfine splittings are in good agreement, though somewhat lower than those in the literature (Table I). There appears to be a solvent effect on the splitting constants as yet quantitatively unpredictable.

Table I. Proton hyperfine splittings in the ESR-spectra of vitamin K_3 intermediates

Method of preparation/solvent	HFs (gauss) at position numbers						Reference
	2	3	5	6	7	8	
red. with Na_2SO_3/H_2O	3.02	2.33	0.66	0.66	0.66	0.66	this work
K_3-sulphonate + OH^-/H_2O							
K mirror/EtOH	2.911	2.467	0.48	0.78	0.56	0.70	[9]
K mirror/EtOH/H_2O	3.01	2.38	0.64	0.64	0.64	0.64	[10]
electrochem. red. OH^-/H_2O	2.94	2.40	0.59	0.59	0.59	0.59	[11]

Table II. Radical anion yields in the system K_3–Na_2SO_3 ($Na_2SO_3 = 10^{-1}$ *M*)

Menadione conc. ($M/l \times 10^{-3}$)	Mean radical 3 on conc. ($M/l \times 10^{-3}$)	Conversion to anion (%)
2.70	2.38	88
1.40	1.30	93
0.70	0.65	92

We conclude, beyond all reasonable doubt, that it is the anion **3** with which we are concerned in these experiments. The role of the anion in the overall chemistry follows from the data summarized in Table II and shows that the reaction

$$K_3 + SO_3^{--} \rightarrow K_3^- + SO_3^- \qquad (1)$$

is essentially quantitative.

These results, taken with the observation for near quantitative sulphitation of **1** by Na_2SO_3, strongly suggest that **3** is an intermediate en route to the sulphonate **2**. Similarly the rapid radical build-up and its exceptional stability suggests that the rate-determining step is the subsequent sulphitation of the radical anion by SO_3^{--}.

Figure 2 shows the ESR-spectra observed on treating the sulphonate with NaOH solution (pH 7–8). Unfortunately we have been unable to interpret the spectrum 2a, except to point out that it is of a completely different nature to that shown in Figure 1 (spectral width of only 5–6 G) and undisturbed by the latter. It can be analyzed on the basis of 2H (aromatic ring protons) – 3H (CH_3) – 2H (aromatic ring protons) interactions leading to overlapping patterns of 2.0, 0.49, 0.14 G hyperfine splittings. We can tentatively ascribe this to a semiquinone derived directly from the sulphonate without fission of the SO_3Na group, where the accidental equivalences present in the **1** anion are removed by this group. It can, however, be said with certainty that a longer reaction-time leads to formation of the **1** anion as observed in Figure 1, possibly in parallel or consecutive reactions but more likely caused by the slow removal of the SO_3Na group by OH^-.

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Structure and Stereochemistry of Coccuvine (*Cocculus laurifolius* DC)

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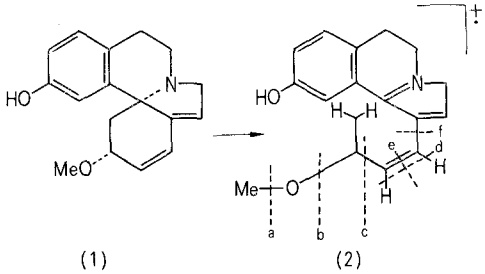
Summary. Coccuvine $C_{17}H_{19}NO_2$, m.p. 137–38°, a new alkaloid from *Cocculus laurifolius* DC has been assigned the structure and stereochemistry as (I) on the basis of spectroscopic studies and chemical correlation.

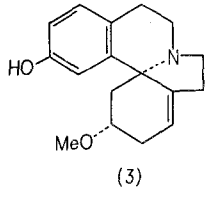
Confirmation of hypotensive activity[1] in *Cocculus laurifolius* DC (Menispermaceae) prompted its reinvestigation, which resulted in the isolation of new dibenz(d,f)-azonine bases[2] and the abnormal *Erythrina* alkaloids[3]. Formerly, from this plant, 1-benzyltetrahydroisoquinoline[4–6], aporphine[7,8], *bis*benzylisoquinoline[9,10] and *Erythrina* alkaloids[11–13] had also been isolated. Continued search for the active principle(s) from the alkaloidal fraction from the leaves of the plant has now yielded a new base named Coccuvine. The present communication reports essential data which have led to the assignment of structure **1** with stereochemistry as shown for the coccuvine.

The phenolic fraction of the alkaloidal mixture from the leaves of *C. laurifolius* DC was carefully chromatographed on neutral Al_2O_3 column. Elution with chloroform/methanol (98:2) yielded coccuvine m.p. 137–38°. The molecular formula $C_{17}H_{19}NO_2$ (M^+ 269) for the base emerged from its elemental analysis[14] and was confirmed by mass spectrometry. Its IR-spectrum had absorption band at 3450 cm^{-1} for a hydroxyl function and the UV-spectrum (λ_{max} 228 and 282 nm) was very similar to that of aromatic *Erythrina* alkaloids[15], having a 1,6-diene system. The NMR-spectrum of the base was almost identical with erysotrine[15] and erythraline[15], the only apparent difference being in the number of signals for methoxyl and methylenedioxy groups. In coccuvine (**1**) there was no signal for an aryl methoxyl function, a 3 proton signal for –CH–O–*Me* resonated at τ 6.74. Of the 3 aromatic protons, 2 *meta* oriented protons were centred at τ 3.24 (J = 2.0 Hz) and an *ortho* oriented proton clear of others at τ 2.92 (1H, d, J = 9.5 Hz); 3 olefinic protons, with one at low field τ 3.45 (1H, d, d, J = 11.0 Hz and J_2 = 2 Hz), the other at τ 4.02 (1H, d, d, J_1 = 10 Hz and

J_2 = 0.5 Hz) forming the 'A' part of the ABX system and the third at τ 4.20. Double resonance experiments[16] enabled us to interprete these data fully. Irradiation at τ 6.50 (α to oxygen) caused a collapse of the small (2 Hz) splitting of the olefinic protons at τ 3.45, leaving the AB system (J = 10 Hz) of the 2 lower field olefinic protons. This infers a *cis* orientation of the double bond. The irradiation also sharpened the signal at τ 4.02 of the 'A' part of the system indicating 0.5 Hz allylic coupling. These results are accommodated by the 3-methoxy-1,6-diene system of the *Erythrina* alkaloids and imply a 3-4-equatorial conformation for the methoxyl group, as is present in the previously characterised *Erythrina* alkaloids[17,18].

The hydroxyl group present in **1** was placed at position C-15 as follows: irradiation at τ 7.09 (benzylic region) sharpened a low field doublet at τ 2.92 due to an *ortho* coupled aromatic proton. There was no effect on the other aromatic protons; irradiation > 10 Hz either side of τ 7.09 had no effect. It follows that the hydroxyl group is at C-15.





The mass fragmentation pattern of the base was in complete agreement with the proposed structure **1**. The prominent ions in the spectrum were *m/e* 269 (M^+); a) 254 ($M^+ - 15$); b) 238 ($M^+ - 31$ base); c) 211 ($M^+ - 58$); d) 209 ($M^+ - 60$); e) 198 ($M^+ - 71$) and f) 185 ($M^+ - 84$). A rationalisation of this, based on established precedent[19] is given in **2**.

Reduction of coccuvine in methanol with 10% Pd/C afforded dihydrococcuvine which was found identical in all respects with cocculine (**3**)[13] of established stereochemistry; coccuvine must, therefore, have the structure and stereochemistry shown in **1**.

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Levels of α_1-Antitrypsin in the Spring and Autumn Seasons

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Summary. In a group of 84 pairs of 11-year-old children of both sexes, the level of the α_1-antitrypsin (α_1-AT) were ascertained in the autumn and spring. Although the mean levels of α_1-AT in the two seasons hardly differed, the highly significant seasonal changes in the distribution curves of α_1-AT values were noted in boys, whereas the levels showed higher stability in girls.

The levels of α_1-antitrypsin (α_1-AT) in the blood serum are genetically determined (for ref. see [1–3]). On the other hand, the α_1-AT levels are concomitantly influenced by a number of intrinsic and extrinsic factors: rising in cases of malignant tumors[4], of different pneumopathies[5], in pregnancy and parturient women[6], in macrophages of smokers[7] and in persons injected with typhoid vaccine[8]. The relevance of low levels for the pathogenesis of obstructive pulmonary disease is well known[1–3]. In view of the potential lability of the α_1-AT levels, we were

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