THE STRUCTURE OF FERULIN

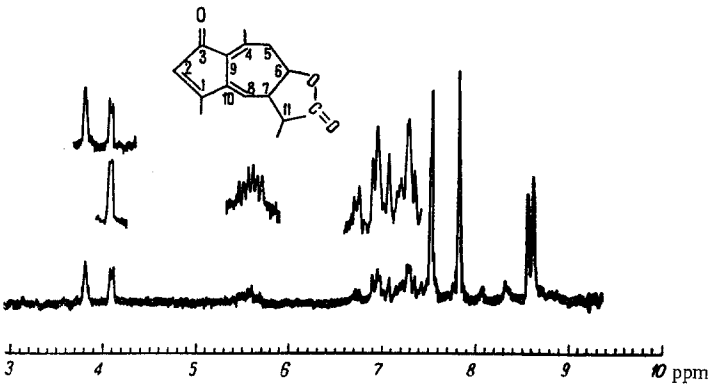
S. V. Serkerov

Khimiya Prirodnykh Soedinenii, Vol. 6, No. 3, pp. 371–372, 1970

UDC 547.913.5+547.4732

Previously [1], on the basis of IR and UV spectra the probable structure I was proposed for ferulin. Ferulin dissolves in alkalis, but in contrast to feropodin [2] it is not isomerized or otherwise changed.

This paper gives the results of an interpretation of the NMR spectrum (figure) of ferulin. The doublet in the spectrum with a center at τ 8.59 (J = 6 Hz, 3H) relates to a CH_3—CH< group in a lactone ring. This also explains the absence from the UV spectrum of a maximum at λ 224–210 mμ [3]. The singlet signals with τ 7.82 and 7.53 (with an area of 3H each) show the presence of two double bonds adjacent to methyl groups of the guaiane carbon skeleton. This determines the position of these double bonds.



NMR spectrum of ferulin.

Since the double bonds are conjugated with the ketone group of a five-membered ring (which is shown by the maxima in the UV spectrum) the position of one double bond may be taken as C_4—C_9 with confidence. According to structure I, the second double bond is trisubstituted and the third is disubstituted. Consequently the total area of the olefinic protons in the NMR spectrum of ferulin should correspond to three protons. However, two signals are found in the spectrum: a singlet at τ 3.82 (1H) and a doublet with a center at τ 4.08 (J = 4 Hz, 1H). If (without taking the nature of the splitting into account) the signals relate to two olefinic protons at C_5 and C_6 then, thanks to the singlet of the vinyl methyl group (τ 7.82 or 7.53), the second double bond is tetrasubstituted, i.e., it is located at C_1—C_{10}. In this case, the proton of the lactone ring should appear in the form of a doublet. Furthermore, a double bond in the α-position would cause a considerable lowering of its chemical shift. The multiplet signal with a center at τ 5.57 (1H) due to the lactone proton corresponds to the C_6—C_7 position. Consequently, the singlet of the CH_3—C group together with the singlet of the olefinic proton at τ 3.82 (1H) shows the presence of a double bond at C_1—C_2. The third double bond, also conjugated, is trisubstituted and can be located only at C_8—C_{10}. This is shown by the doublet of an olefinic proton with its center at τ 4.08 (J = 4 Hz, 1H).

Thus, ferulin is 3-oxoguai-1(2),4(9),8(10)-trien-6,12-olide.

The NMR spectrum was taken in deuterochloroform on a JNM-4H-100 instrument with tetramethylsilane as the internal standard.

REFERENCES

1. S. V. Serkerov, KhPS [Chemistry of Natural Compounds], 6, 134, 1970.
2. S. V. Serkerov, KhPS [Chemistry of Natural Compounds], 5, 245, 1969.

3. S. V. Serkerov, KhPS [Chemistry of Natural Compounds], 5, 241, 1969.

16 February 1970

Komarov Institute of Botany, AS AzerbSSR