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Structure of Elsholtzidiol, a New Bisubstituted Furan of *Elsholtzia densa* Benth

During the course of systematic investigation of the essential oils of *Elsholtzia* species, a number of furan compounds were isolated. A crystalline solid was isolated by column chromatography of the essential oil of *E. densa* Benth.[1] and named elsholtzidiol.

The essential oil, obtained in 0.3% yield by hydrodistillation of this plant, was chromatographed over Brockman alumina (grade II) and the title compound was obtained in a yield of 5.1% from the ether eluted fractions. Repeated crystallizations from petroleum ether (40–60°) gave white crystalline needles, mp 58–59°, a single spot of Rf 0.36 on TLC (silica gel G; 50% ethyl acetate in benzene). The purity of the compound was also verified by GLC. The elemental analysis conforms to the molecular formula $C_{10}H_{16}O_3$, M^+ 184. In the UV-region it gave λ_{max} 218 nm characteristic of furan compounds. The IR-spectrum[2,3] showed principal peaks at 3378 cm^{-1} (OH, broad and intense), 1296, 1275, 1218 and 1157 cm^{-1} (due to 2 hydroxy groups one secondary and the other tertiary); 1512, 1056, 1022, and 882 cm^{-1} (furan ring) and at 1380 and 1355 cm^{-1} (gem dimethyl).

The NMR-spectrum (100 Mc; $CDCl_3$) was in agreement with structure (Figure 1) and all the protons are at expected positions. The position of the 2 hydroxy protons was confirmed with D_2O exchange. The NMR also showed a characteristic pattern of an ABX system[4] (Figure 2).

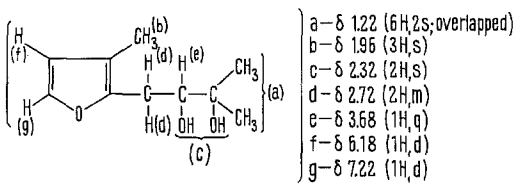

Fig. 1. Structure of Esholtzidiol.

[1] J. D. Hooker, *Flora of British India* (L. Reeve and Co., Covent Garden, London 1885), vol. IV, p. 645.

[2] K. Nakanishi, *Infrared Absorption Spectroscopy* (Holden-Day, Inc. San Francisco and Nankodo Co., Ltd., Tokyo 1966), p. 30, 52 and 197.

[3] H. A. Szymanski, *Interpreted I.R. spectra* (Plenum Press, Data Division, New York 1966), vol. 2, p. 281.

[4] N. S. Bhacca and D. H. Williams, *Application of NMR spectroscopy in Organic Chemistry* (Holden-Day, Inc. San Francisco 1966), p. 46.

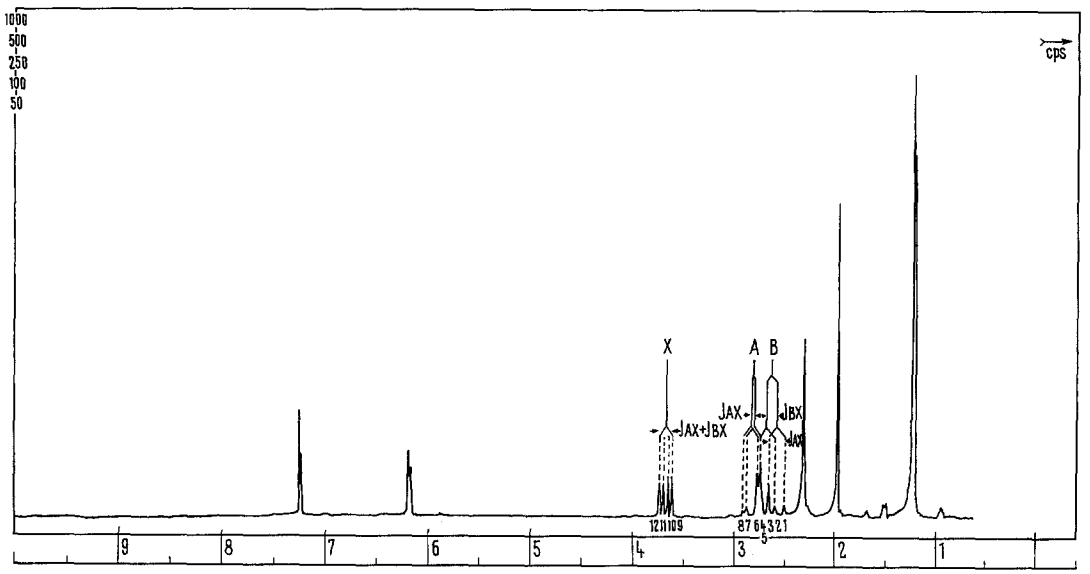

Fig. 2. NMR-spectrum of Esholtzidiol.

The proposed structure was also confirmed by mass spectroscopy[5]. The molecular ion peak of elsholtzidiol was obtained at m/e 184 and other characteristic peaks at m/e 169, 166, 151, 95, 89, 71 and 65 support the proposed structure (Figure 3). That one of the hydroxy groups is secondary and the other tertiary, was further confirmed by obtaining only a monoacetate of elsholtzidiol. The acetate (n_D^{32} 1.4682) on elemental analysis was found to contain C, 63.67; H, 8.02% (required for $C_{12}H_{18}O_4$ C, 63.72; H, 7.96%). The IR gave bands at 3365 cm^{-1} (OH group) and 1730 and 1247 cm^{-1} (CH_3–CO–OR)[6].

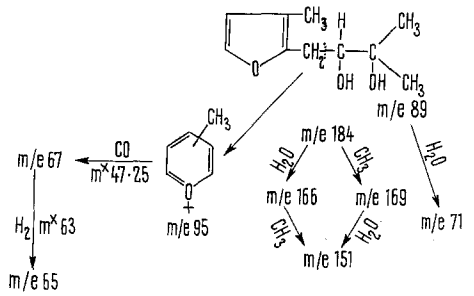

Fig. 3. Mass spectrum of Esholtzidiol.

Zusammenfassung. Isolierung und Strukturaufklärung von Esholtzidiol, einem Pflanzeninhaltsstoff aus *Esholtzia densa* Benth.

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Regional Research Laboratory, Jammu (India), 2 February 1970.

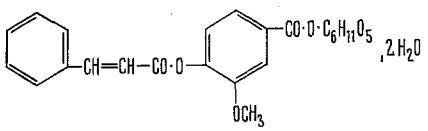
[5] K. HEYNS, R. STUTE and H. SCHARMANN, Tetrahedron *22*, 2223 (1966).

[6] We wish to express our gratitude to Dr. V. S. GUPTA of University of Saskatchewan for elemental analysis, NMR- and IR-spectra; Dr. D. H. G. CROUT of University of Exeter for mass spectrum and Dr. K. GANAPATHI, Director, Regional Research Laboratory, Jammu for his keen interest in this investigation.

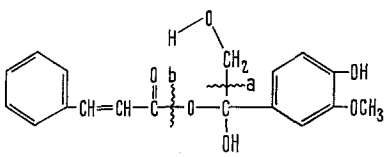
Chemistry of Kutkin, Isolated from *Picrorhiza kurroa* Royle ex Benth

RASTOGI et al.[1,2] previously isolated from the roots of *Picrorhiza kurroa* Royle ex Benth (Scrophulariaceae)[3] a bitter glucoside, kutkin, $C_{23}H_{24}O_{10}$, $2H_2O$, mp 211°, $[\alpha]_D^{41}$ — 165°, together with D-mannitol, vanillic acid, and several uncharacterized products. Kutkin, on hydrolysis, yielded vanillic acid, cinnamic acid and glucose, on the basis of which they put forward structure (I) for kutkin. In view of the uses of the drug reported in the indigenous and modern systems of medicine[4,5], we became interested in the chemistry of kutkin which appeared to be the active principle of the drug. Moreover, the structure (I) proposed for kutkin by RASTOGI et al. is not consistent with the biogenetic principles applicable to lignins[6], known to be derived from C_6 to C_3 and D-glucose precursors. Again, the facile hydrolysis of kutkin to glucose and other fragments in protic solvents, even at ordinary temperatures, also militates against the assumption[1] that the phenolic and sugar entities are joined in an ester linkage as shown in (I).

Materials and methods. The acid hydrolysate of kutkin, obtained by treating it with dilute hydrochloric acid, at room temperature, exhibited on papergrams 2 spots at Rf, 0.77 and 0.87, due to 2 reducing entities, besides the one at Rf, 0.26, due to glucose. The glucoside itself did not contain any reducing function. These results indicate that during the liberation of glucose from kutkin under mild acid treatment, the resultant aglycone develops 2 reducing entities, (A) and (B), having Rf, 0.77 and 0.87, respectively. The ratio of (A) to (B) also varied (ranging from 70 to 90) depending on the conditions of hydrolysis. The component (B) was isolated from the aqueous acidic solution by extraction with chloroform and from the mother liquor, (A) was later obtained by extraction with *iso*-amyl alcohol. Both the compounds on further hydrolysis, however, gave the same 2 products, viz. cinnamic and vanillic acids. Attempts to dry a sample of (A) over



(I)



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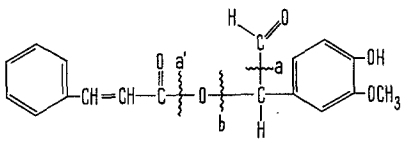

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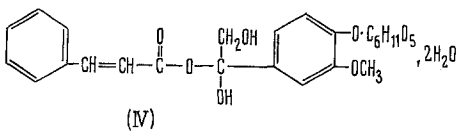

(IV)

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