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THE STRUCTURE OF A NEW POLYTHIENYL FROM ECLIPTA ALBA

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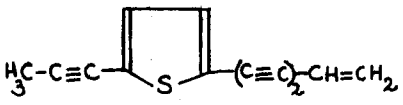
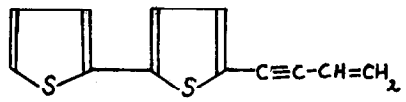
Eclipta alba (Compositae) has been known to contain nicotine (1), wedelolactone (2) and desmethylwedelolactone besides sulphur containing peptides (3). Recently, Bohlmann and co-workers (4) detected the presence of two thiophene derivatives (I) and (II) and the polyacetylene (III) in this plant.



I



II

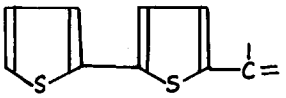
$$CH_3-(C\equiv C)_5-CH=CH_2$$

III

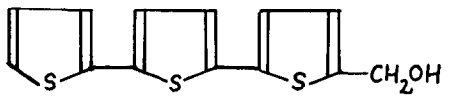
We have now isolated a new polythienyl whose properties are reported in this communication. A petroleum ether extract of the dry leaves (2 kg) was hydrolysed with methanolic alkali, diluted and extracted with ether leaving behind chlorophyll in the alkaline solution. The chlorophyll-free, neutral residue (ca. 5 g) from the ether extract was dissolved in light petroleum-ether mixture

and chromatographed over deactivated alumina (5). The column was developed with light petroleum (40-60°) and the various bands eluted with it containing increasing amounts of ether. Light petroleum-ether (25%) eluate yielded stigmasterol (500 mg). The subsequent eluates richer in ether yielded a sulphur compound, lemon yellow plates (80 mg), from benzene, m.p.150-151°. It analysed for $C_{13}H_{10}S_3O$, λ_{max}^{MeOH} (ε) 250 mμ (6,166), 355 mμ (15,490). Acetate, m.p. 114-116°, λ_{max}^{MeOH} (ε) 252 mμ (7,803), 350 mμ (18,740). Its UV spectrum, colour reactions and marked blue fluorescence in solutions indicated that it might be a derivative of α-terthienyl (6). ν_{max}^{KBr} 3700-3450, 1450, 1425, 1390, 1190, 1160, 1060, 1045, 985, 895, 885, 835, 830, 815, 800, 790, 697, 685 cm^{-1} was characteristic of thiophenes (7). The doublet near 840 cm^{-1} indicated the presence of at least one mono (α) substituted thiophene unit (8). The NMR spectrum in $(CD_3)_2$ SO had the following features: a broad signal at τ 5.42-5.50 (one alcoholic OH proton), a sharp signal at τ 4.99 (2 Ar-CH_2-O-protons) and a complex multiplet at τ 2.05-2.75 (7 thiophene protons). The compound (10 mg) was completely oxidised by potassium permanganate in acetone at room temperature (9). TLC of the acidic product showed the presence of two components, one giving bluish-green colour with the sulphuric acid spray and the other pink. The UV spectrum had a very intense maximum at 272 mμ and

another of lower intensity at 332 mμ and indicated that it might be a mixture of thiophene 2,5-dicarboxylic acid and bithienyl-α-carboxylic acid (9,10) in the proportion 5:1. The identity was confirmed by comparison (spectral and TLC) with authentic specimens of the two acids. This result proved the presence of the partial unit (IV). Taking into consideration the other properties and in particular the UV and NMR spectral data, the complete structure of the compound would be α-terthienylmethanol (V).



IV



V

This new alcohol could not be detected in the related plant, Wedelia calendulaceae which has, however, yielded stigmasterol and β-amyrin; further work on the other components of the two plants is in progress. The unstable compounds(I,II) detected by Bohlmann and co-workers (4) in E. alba might have been lost due to polymerization in the process of our extraction.

Acknowledgements

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REFERENCES

1. S.N.Pal and M.Narasimhan, J. Ind. Chem. Soc., 20, 181 (1943).
2. T.R.Govindachari, K.Nagarajan and B.R.Pai, J. Sci. Industr. Res., 15B, 664 (1956).
3. N.R.Krishnaswamy, Ph.D. Thesis, Delhi University, 1962.
4. F.Bohlmann, K.M.Kleine and C.Arndt, Chem. Ber., 97, 2125 (1964).
5. T.W.Goodwin, Biochem. J., 50, 550 (1952).
6. L.Zechmeister and J.W.Sease, J. Amer. Chem. Soc., 69, 273 (1957).
7. A.R.Katritzky and A.J.Boulton, J. Chem. Soc., 3500 (1959).
8. H.D.Hartough, Thiophene and its derivatives, p.115 Interscience, New York (1952).
9. J.H.Uhlenbroek, and J.D.Bijloo, Rec. trav. chim., 78, 382 (1959).
10. S.Gronowitz, Arkiv. Kemi, 21, 265 (1963).