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THE STRUCTURE OF MUNETONE

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MUNETONE, an isoflavone constituent of Mundulea suberosa of the family Leguminosae, was isolated by Dutta[1] who assigned to it the molecular formula $C_{21}H_{18}O_4$ and the structure I. Since the absence of an oxygen substituent at the 4'-position would make munetone unique among the numerous isoflavonoids which have so far been isolated from the Leguminosae,[2] the structure of munetone has been re-examined. The mass spectrum of munetone gave a strong molecular ion at $^m/_e416$ with a measured isotopic abundance ratio $(^{417}/_{416})$ of 0.287, corresponding to the molecular formula $C_{26}H_{24}O_5$, and

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[1] N. L. Dutta, J. Ind. Chem. Soc. **33**, 716 (1956); Ibid. **36**, 165 (1959).

[2] W. D. Ollis in The Chemistry of Flavonoid Compounds p.353, ed. by T. A. Geissman. Pergamon, Oxford (1962).

not $C_{21}H_{13}O_4$. The elementary analyses reported earlier[1] for munetone and its derivatives, including the deoxybenzoin (munetol), are equally in agreement with the two formulae; the methoxyl values, now re-determined, are closer to those required for the larger molecule. The replacement of the B ring by a 2,2-dimethylchromene ring system will account for the difference in the molecular formulae.

The loss of CH_3 from the molecular ion of munetone gives the base peak $^m/_e 401$ having an intensity five times that of the molecular ion. This is in quantitative agreement with the observed[3] fragmentation of 2,2-dimethylchromenes which may thereby give stable benzopyrylium ions. A series of doubly charged ions (e.g. one at $^m/_e 193$ corresponding to 386^{++}) are best accounted for on a bis-dimethylchromene structure. The mass spectrum of munetol shows the parent ion at 406, corresponding to $C_{25}H_{26}O_5$, a deoxybenzoin from an isoflavone $C_{26}H_{24}O_5$. A fission giving two peaks of equal mass number 203 and a doubly charged ion (376/2 = 188) resulting by loss of 15 + 15 from the parent ion were also indicated.

In the light of the structure II of mundulone[4] which occurs in the same plant, it is reasonable to assume that munetone is constituted as III. In its mass spectrum mundulone shows a close similarity to munetone by the peaks at 416, 401, 385, 371 and the doubly charged ion at 193. The molecular ion shows at 434, while 416 (p-18) (munetone) arises by loss of water, and 419 (p-15) by loss of methyl

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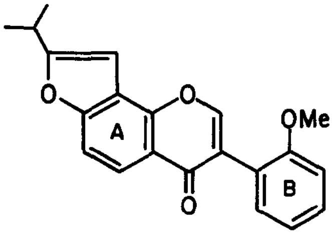
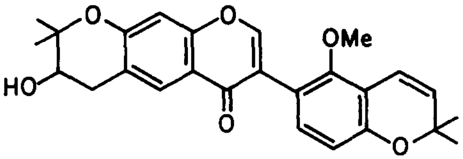
[3] C. S. Barnes and J. Occolowitz, unpublished observations.

[4] B. F. Burrows, N. Finch, W. D. Ollis and I. O. Sutherland, Proc. Chem. Soc. 150 (1959); A. C. Ghosh and N. L. Dutta, J. Ind. Chem. Soc. **39**, 475 (1962).

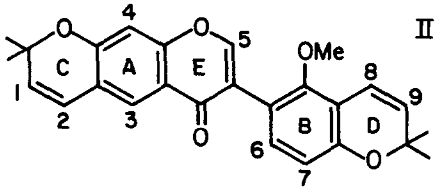
from the molecular ion. Peaks at 245, 273, 288 are not present in munetone and probably arise because of the different fragmentation produced by the hydroxy-dimethylchroman ring.



I



II



III

The NMR spectrum and chemical evidence have fully confirmed structure III for munetone.

The NMR spectrum of munetone gives a total proton count of 24 and shows two pairs of gem-dimethyl groups at τ = 8.51 and 8.55, the expected place for Me of 2,2-dimethylchromene systems.[5,6] The observed small separations between these

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[5] B. F. Burrows, W. D. Ollis and L. M. Jackman, Proc. Chem. Soc. 176 (1960).

[6] L. Crombie and J. W. Lown, J. Chem. Soc. 775 (1962).

peaks, as well as the lack of a single proton septet, indicate the absence of an isopropyl group. These facts are in agreement with III, and at variance with I which has an isopropyl group and only 18 protons. Moreover, a relatively complex band, which is not observed, is expected in the aromatic region from the four adjacent protons of ring B in I.

The assignments for the low field absorptions are given in Fig. 1; the numbering of the protons is marked in III. H_3, which comes under the deshielding influence of the CO group, has to be[6] one of the two protons at 2.05 and 2.10 and is therefore a singlet; it cannot have an ortho H in agreement with III. The second proton of this group has to be H_5, which is β to the CO group and comes under the deshielding influence of both aromatic rings. The singlet single proton absorption at 3.18 may be assigned to H_4. The peaks at 3.28, 3.43 and 3.60 have the intensity ratio of 1:1.5:0.5 with a spacing of 9-10 cps between them. The pair of doublets centered at 4.25 and 4.33 with a coupling constant of 10 cps are in the expected place for the β-proton of 2,2-substituted chromene systems.[5,6] The corresponding α-protons (H_2, H_8), together with an aromatic proton having an ortho neighbour (H_6 or H_7), give rise to the group of peaks at 3.28, 3.43 and 3.60. The pair of doublets centered at 3.35 and 3.50 may be assigned to the chromene α-protons. The remaining doublet of this group, along with the one centered at 2.84, represents a pair of ortho coupled protons (H_6 and H_7); the absorption at the lower field must be assigned to H_6 whose environment is

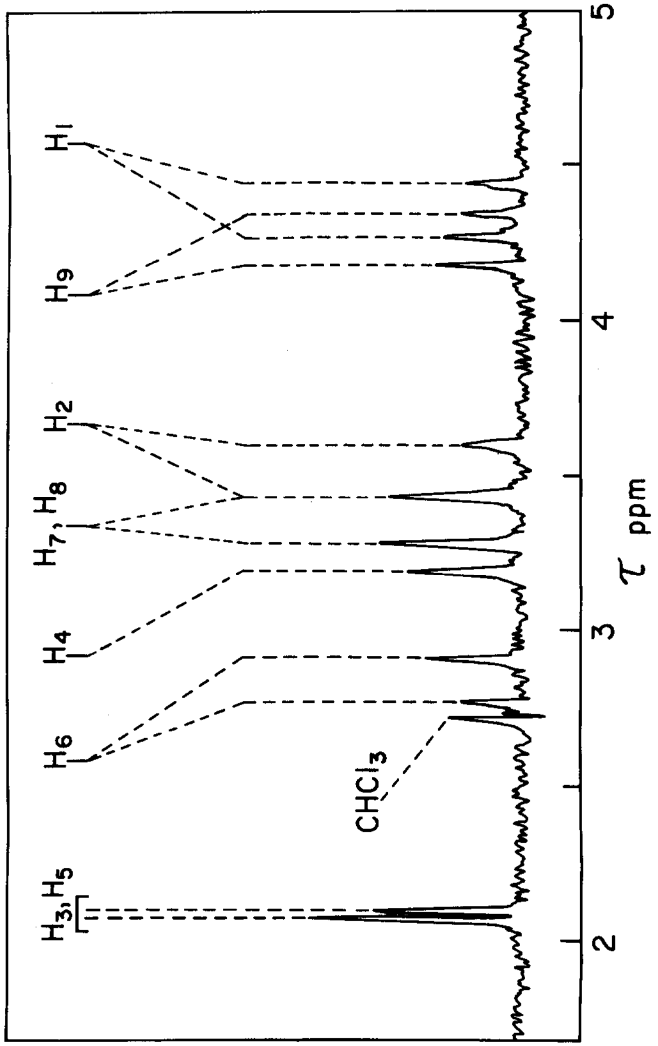

FIG. 1

NMR spectrum of munetone.

close to that of a plain aromatic proton, and the signal at the higher field to H_7 which has an ortho oxygen atom.[7]

The spectrum of mundulone, the low field part of which is shown in Fig. 2, where one pair of chromene doublets is missing, confirms the assignments in the munetone spectrum, and makes possible the identification of the chromene proton resonances (H_1, H_2, H_8, H_9) as given in Fig. 1.

In presence of 10 per cent Pd/C in glacial acetic acid munetone absorbed one molecule of hydrogen in 10 min, and two in an hr. The crude product contained an isoflavanone because it gave a dinitrophenylhydrazone; but the recrystallized material, m.p. 183-184°, was identical with the isoflavone obtained by cyclization of tetrahydromunetol, readily obtained by catalytic hydrogenation of munetol, with ethyl orthoformate and piperidine.[8] This tetrahydromunetone, like other isoflavones, did not form a dinitrophenylhydrazone. Hydrogenation of munetone with the Adams catalyst in glacial acetic acid yielded hexahydromunetone, m.p. 157°, which was an isoflavanone and formed a dinitrophenylhydrazone.

Acetone, obtained in very poor yield, was identified as the volatile product when munetone was hydrolyzed with 5 per cent aqueous sodium hydroxide at 100°; although the formation of acetone by mild hydrolytic fission is a general property of 2,2-dimethylchromenes, exceptions such as

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[7] J. B. Bredenberg and J. N. Shoolery, Tetrahedron Letters No.9, 285 (1961).

[8] V. R. Sathe and K. Venkataraman, Curr. Sci. **18**, 373 (1949).

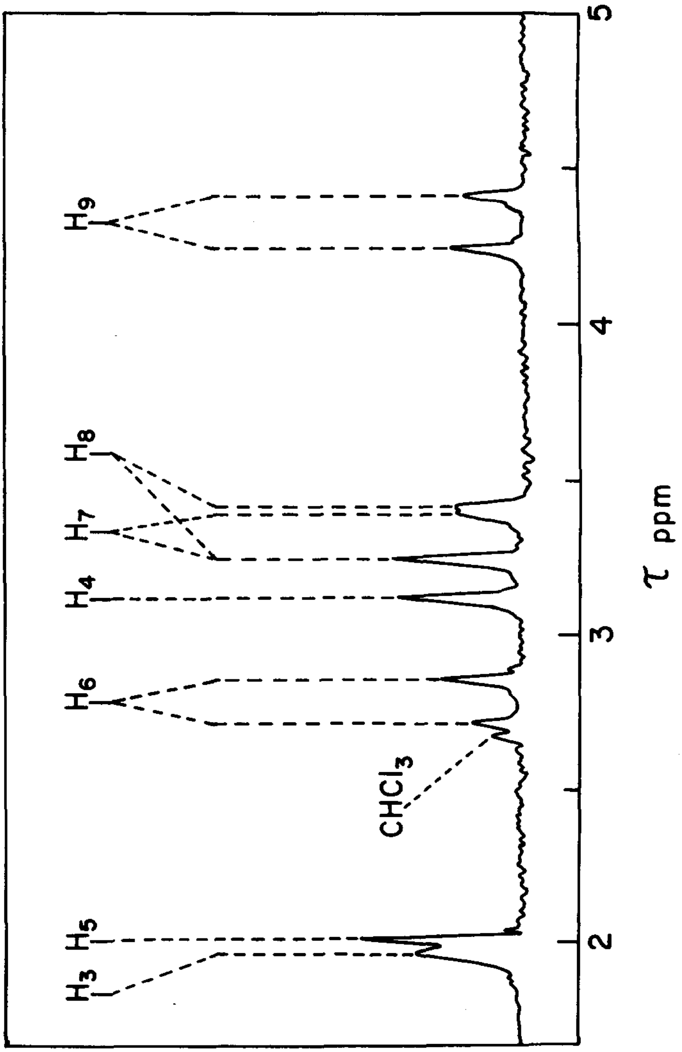

FIG. 2

NMR spectrum of mundulone.

jamaicin have been recorded in the literature.[9] Alkali fusion of tetrahydromunetol with potassium hydroxide at 250° led to 7-hydroxy-2,2-dimethylchroman, identified by direct comparison with a synthetic specimen.[10]

Attempts to dehydrate mundulone (II) to munetone (III) by prolonged refluxing with dimethylsulphoxide[11] or phosphorus pentoxide and ethanol[12] were unsuccessful. Munetone is not an artefact formed from mundulone during chromatography on alumina, which was used for its isolation, because mundulone was unaffected by similar treatment. We believe that the biogenetic relationship of mundulone and munetone is the hydration of the latter rather than the dehydration of the former.[13]

The synthesis of tetrahydromunetol and hexahydromunetone is in progress.

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[9] O. A. Stamm, H. Schmid and J. Büchi, Helv. Chim. Acta 41, 2006 (1958).

[10] H. B. Bhat and K. Venkataraman, Tetrahedron (1962), under publication.

[11] V. J. Traynelis, W. L. Hergenrother and J. R. Livingston, J. Org. Chem. 27, 2377 (1962).

[12] T. Mukaiyama and T. Hata, Bull. Soc. Chim. Japan 34, 99 (1961).

[13] Cf. W. D. Ollis and I. O. Sutherland in Recent Developments in the Chemistry of Natural Phenolic Compounds p. 98. Pergamon, Oxford (1962).