References

1. S. TAKEDA and M. ABURADA, *J. Pharmacobio-Dyn*, 1981, 4, 724.
2. C. H. YANG, C. CHIANG, K. LIU, S. PENG and R. WANG, *Chem. Abstr.*, 1981, 95, 161758.
3. A. TYAGI, V. P. DIXIT and B. C. JOSHI, *Naturwissenchaften*, 1980, 67, 104.
4. A. A. DEANA, *J. Med. Chem*, 1983, 26, 580.
5. M. HEALEY and R. ROBINSON, *J. Chem. Soc.*, 1934, 1626.
6. N. M. SHAM and R. C. SHAH, *Chem. Ber.*, 1938, 71, 2075.

Nuclear Magnetic Resonance Study on some 4-Methoxyacetophenones

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THE study of the electrical dipole moment of certain anisoles and thioanisoles led to the discovery of a new effect termed steric enhancement of resonance[1] (SER). Many papers based on physicochemical properties of suitably substituted anisoles and thioanisoles were published[2] providing evidence for the aforesaid effect. We have recorded and analysed the pmr data of some alkyl- and halogeno-methoxyacetophenones to gain evidence for the newly observed effect.

All the compounds described in Table 1 were prepared by known standard procedures.

TABLE 1—PMR CHEMICAL SHIFTS (δ) OF SOME ACETOPHENONES*

Acetophenones	Methoxyl	Acetyl-methyl	Aryl-methyl
Acetophenone	–	2.6 (2.5)	–
4-Methoxy	3.92 (3.8)	2.51 (2.4)	–
4-Methoxy-3-methyl	3.86 (3.8)	2.52 (2.0)	2 23 (2.5)
3-Fluoro-4-methoxy	3.92 (4.0)	2.51 (2.2)	–
3-Chloro-4-methoxy	3.94 (4.0)	2.53 (2.1)	–
3-Bromo-4-methoxy	3.92 (4.0)	2.51 (2 0)	–
3-Iodo-4-methoxy	3.95 (3.9)	2.55 (1.8)	–
4-Methoxy-3,5-dimethyl	3.74 (3.8)	2.50 (2 6)	2 29 (2.7)
3,5-Dichloro-4-methoxy	3.98 (4.0)	2.58 (2 6)	–
3,5-Dibromo-4-methoxy	3.99 (4.0)	2.58 (2.6)	–

*Values in parentheses from Ref. 6.

Nmr chemical shifts have been extensively used as probes of electronic substituent effects[3,4]. Heathcock[5] has analysed the influence of the substituents on the chemical shifts of the alkoxyl hydrogen of anisoles and phenetoles. The data indicate that in *ortho*-substituted-anisoles the methoxyl protons have higher chemical shift values (downfield) than those of the corresponding *para*-substituted-anisoles, irrespective of whether the substituent is electron-donor or electron-acceptor. This can be explained on the basis of SER.

The pmr data on some methoxyacetophenones are recorded and presented in Table 1. We have analysed the sensitivity of methoxyl hydrogen and acetyl hydrogen shieldings to substitution in aromatic ring. It is found that the methoxyl hydrogen resonance is not significantly affected when further substitution takes place either in 3-position or in 3- and 5-positions of 4-methoxyacetophenone eventhough the value changes when we go from anisole to 4-methoxyacetophenone. Similarly, all the compounds studied have more or less the same chemical shift values for the acetyl group. Therefore, we failed to get any useful information about the operation of ser from the above analysis on pmr data.

However, there is a recent report by Ganapathy and Ramanujam[6] on the pmr spectral data of the compounds of interest, in which they claimed that the acetyl proton shift in the compounds furnishes evidence for SER. Their data are also presented in parenthesis in Table 1. The assignment of the signal for acetyl proton by the above authors of the compound 4-methoxy-3-methylacetophenone seems to be erroneous. They have assigned the signal at δ 2 0 to methyl proton of the acetyl group and δ 2.5 to the 3-methyl group, we feel that it might be the other way. We assigned the peak at δ 2.52 to methyl of acetyl group and at δ 2.23 to the 3-methyl group. When we compare the monosubstituted- and trisubstituted-acetophenones, it is obvious that acetyl group should have value approximately δ 2.5. Moreover, it is claimed that the chemical shift of acetyl group value gradually decreases from 3-fluoro- to 3-bromo- to 3-iodo-4-methoxyacetophenone. However, in our determination we obtained almost the same values (Table 1) and a decreasing trend has not been observed. The values we got are more reliable because they have been taken from the computer print-out of the nmr machine (JEOL FX Q90). It is concluded from our observations that the substituent chemical shift either on acetyl proton or methoxyl proton is not that much sensitive to realise the new effect. We fail to understand why the chemical shift values for the acetyl methyls and the aryl methyl (in one case) of the different compounds, as observed by us, differ so much from those reported by Ganapathy and Ramanujam[6].

References

1. V. BALIAH and M. UMA, *Tetrahedron Lett.*, 1960, 25, 21.
2. V. BALIAH and P. V. V. SATYANARAYANA, *Indian J. Chem., Sect. A*, 1984, 23, 883, and references cited therein.
3. D. F. EWING in "Correlation Analysis in Chemistry—Recent Advances", eds. J. SHORTER and N. B. CHAPMAN, Plenum Press, New York, 1978, Chap. 8.
4. W. J. HEHRE, R. W. TAFT and R. D. THOMSON, *Prog. Phys. Org. Chem.*, 1976, 12, 159.
5. C. HEATHCOCK, *Can. J. Chem.*, 1962, 40, 1965.
6. K. GANAPATHY and M. RAMANUJAM, *J. Indian Chem. Soc.*, 1983, 60, 958.

Chemical Constituents of *Polycarpone loeflingiae*†

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POLYCARPONE loeflingiae edgew HKf, syn. *P. prostratum*, belonging to family Caryophyllaceae is found throughout the hotter part of India in fields and waste lands. It is also distributed in tropical Asia and Africa[1]. There appears to be no work carried out on the genus *Polycarpone* in general and on *P. loeflingiae* in particular. This is the first report on the chemical constituents of *P. loeflingiae*. Under our programme of screening Indian plants for a wide range of biological activity, 50% alcoholic extract of the whole plant (aerial parts only) of *P. loeflingiae* showed good spasmolytic activity[2] (75% inhibition of $BaCl_2$ induced spasm at 50 $\mu g\ ml^{-1}$ concentration) and was taken up for detailed chemical investigation.

The plant material (aerial parts only) was collected from Chilapata, Jalpaiguri, West Bengal, India in March 1982 by the Botany Division of C.D.R.I. (Lucknow) and a voucher specimen of the same is preserved in the herbarium of the Institute.

The shed-dried whole plant (3 kg dry weight) was powdered and extracted with 90% ethanol at room temperature by percolation method. The total alcoholic extract concentrate was successively fractionated with hexane and chloroform. The resulting residue was taken up in methanol and filtered to remove the inorganic salts. The three well defined fractions, hexane soluble, chloroform soluble and methanol soluble thus obtained were chromatographed separately over silica gel column to yield the following compounds.

The hexane soluble fraction on chromatography yielded hentriacontane (i), m.p. 68°; hentriacontanol (ii), m.p. 84–6°; β-amyrene (iii), m.p. 206–10°, its acetate, m.p. 210–82°; and a sterol mixture (iv) resolved into β-sitosterol and stigmasterol on chromatography of their acetates on $AgNO_3$ impregnated silica gel plates.

The chloroform soluble fraction yielded additional quantities of β-amyrene (iii) and the sterol mixture (iv), alongwith two tetrahydroxytriterpenes: (v), m.p. 285–87° (vi), m.p. 256–60°; and β-D-glucoside of β-sitosterol (vii), m.p. 280–85°. The identity of (v) was confirmed as saikogenin-A (3β, 16β, 23, 28-tetrahydroxyolean-11,13-diene) by comparing its ir, uv, nmr and ms with those reported literature[3], and preparation of diacetonyl derivative, m.p. 200-01° (lit.[3] 201–04°). While (vi) was found to be its 16α-hydroxy-isomer, saikogenin-D (3β,16α,23,28-tetrahydroxyolean-11,13-diene)[3].

The methanol soluble fraction of the alcoholic extract on chromatography yielded a pure saponin, carponoside-A (viii), m.p., 172–74°. On acid hydrolysis (10% methanolic sulphuric acid) carponoside-A yielded the genin $C_{30}H_{48}O_4$, m.p. 256–60°, $[\alpha]_D$–42° (*c*, 1.0 EtOH); λ_{max} 240, 250 and 262 nm; and was identified as saikogenin-D (3β,16α,23,28-tetrahydroxyolean-11,13(18)-diene) and the sugars were identified as glucose and arabinose by pc from the aqueous hydrolysate. Thus, carponoside-A is a new saponin different from saikosaponins of diene type reported[4,5] so far. The presence of these triterpenoids both in the free state as well as saponins (carponoside-A) in *P. loeflingiae* (Caryophyllaceae) are of taxanomic interest since these triterpenoids were first isolated[3] as artifacts of saikosaponins-A and -D from *Bupleurum falatum* belonging to Umbelliferae. The existence of these saponins with olean-11,13(18)-diene system were later reported in other species *Bupleurum rotundifolium*[5]. None of the above reported compounds showed spasmolytic activity.

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References

1. "Wealth of India, Raw Materials", C.S.I.R., New Delhi, 1969, Vol. VIII, p. 189.
2. B. S. ASWAL, D. S. BHAKUNI, A. K. GOEL, K. KAR, B. N. MEHROTRA and K. C. MUKHERJEE, *Indian J. Exptl. Biol.*, 1984, 22, 312.
3. T. KUBOTO, F. TONAMI and H. HINOH, *Tetrahedron*, 1967, 23, 3333.
4. H. ISHI, M. NAKAMURA, S. SEO, K. TORI, T. TOZYO and Y. YOSHIMURA, *Chem. Pharm. Bull.*, 1980, 28, 2367.
5. Y. KOBAYASHI, T. TAKEDA and Y. OGHARA, *Chem. Pharm. Bull.*, 1981, 29, 2222.

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