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SHORT COMMUNICATION

# THE IDENTIFICATION OF THEOGALLIN AS 3-GALLOYLQUINIC ACID

G. V. STAGG and D. SWAINE

Brooke Bond Liebig Research Centre, Blounts Court, Sonning Common, Reading, Berks, RG4 9NZ

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**Abstract—The structure of theogallin, found in unprocessed tea leaf, was confirmed as 3-galloylquinic acid by NMR spectroscopy.**

## INTRODUCTION

THEOGALLIN is a phenolic acid which occurs in the tea plant.[1] It is largely consumed during tea fermentation[2] and may be incorporated into the pigments of black tea.[3] The compound was characterized as a monogalloylquinic acid[4] although other evidence seemed to conflict with this finding.[5] The synthesis of 3-galloylquinic has been reported[6] but its relationship with theogallin was not investigated. The structure of theogallin was not conclusively established in the earlier work; in this communication a highly purified sample of theogallin obtained from unprocessed tea leaf by partition chromatography on cellulose[7] was subjected to NMR analysis.

## RESULTS AND DISCUSSION

NMR data are given in Table 1. The first four signals obtained were consistent with the seven non-exchangeable protons on a quinic acid residue, and the integrals obtained from them were close to the required ratio of 4: 1: 1: 1. These signals were subjected in turn to spin-decoupling by double irradiation. When the four protons at 2·8 δ were irradiated, a very simple spin system remained with coupling constants ($J$) of 7·5 Hz (6·2 δ) and 3 Hz (4·8 6) while the signal at 4·3 δ remained a doublet of doublets. Results of spin-decoupling at 4·3 δ, 4·8 δ and 6·2 δ were consistent with a quinic acid type structure with protons on five adjacent carbon atoms. The doublet of doublets at 4·3 δ is attributable to the proton at C-4 of the quinic acid ring; its presence at midfield indicates that the ring is not substituted at this position.

The coupling factors, in close agreement with those quoted for 3-caffeoylquinic acid,[8] were $J$ (3-4) = 8 Hz, $J$ (4-5) = 3 Hz. It is known[9] that vicinal coupling of 6-membered

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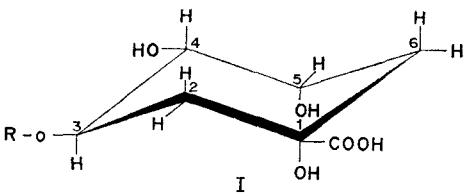
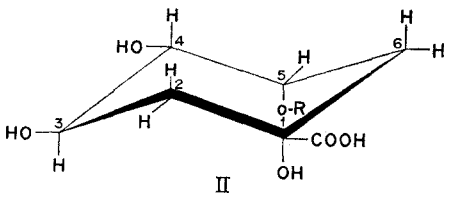
[7] L. VUATAZ and H. BRANDENBERGER, *J. Chromatog. 2, 173 (1959).*
[8] A. C. WAISS, R. E. LUNDIN and J. CORSE, *Chem. & Ind.* 1984 (1964).
[9] R. U. LEMIEUX, R. K. KULLNIG, H. J. BERNSTEIN and W. G. SCHNEIDER, *J.* Am. *Chem. Soc. SO, 6098* (1958).

rings are in the region of 10 Hz for axial-axial (a-a) couplings and 4 Hz for axial-equatorial (a-e) and equatorial-equatorial (e-e) couplings. The coupling therefore between the proton at 6·2 S (designated H3) and that at 4·3 (H4) is a-a, and that between H4 and the proton at 4·8 S (H5) is a-e or e-e.

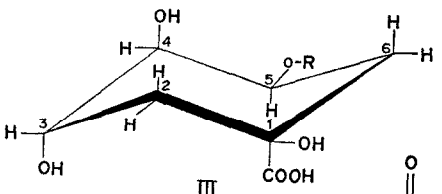
These data are consistent with the conformation resulting from linkage of one galloyl residue at the C-3 position of the quinic acid ring (I). The 5-galloylquinic acid structure (II) has H3–H4 coupling of a-a, but would be expected to have coupling constants of 3Hz (6·2 S) and 7·5 Hz (4·8 δ) on decoupling at the 2- and 6-positions (2.8 S). The optical antipode of 5-galloylquinic acid (III) has e-e coupling between H3 and H4 and is clearly inconsistent with the NMR data. (Furthermore, on thermodynamic grounds it would



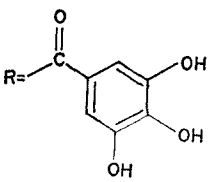

I




II




III




appear that 3-galloylquinic acid affords the most stable configuration, with both the galloyl group and the quinic acid carboxyl function in unhindered equatorial positions.) This is analogous to the chlorogenic acids, of which 3-caffeoylquinic acid is the most abundant.[4,8]

When a full spectrum was determined at 80" a significant increase in resolution was achieved. The exchangeable proton signal was moved upfield to 7·2 δ, enabling the aromatic singlet at 7·7 S to be resolved. The integrals were in the ratio 50: 14: 12: 13 : 24; very close to the ratio 4: 1: 1 : 1 : 2 required for monogalloylquinic acid structure. The fact that the signal for the aromatic ring resulted from 2 protons but was unsplit indicates that they are equivalent with the moiety probably having an axis of symmetry. This is in accordance with the proposed structure I.

TABLE 1. NMR DATA FOR THEOGALLIN (IN DEUTEROPYRIDINE; TMS AS INTERNAL STANDARD; AMBIENT TEMPERATURE)

| δ(ppm) | Integral | Attributed to |
|---|---|---|
| 2·8 | 16 | Aliphatic protons |
| 4·3 | 5 | Aliphatic protons adjacent to oxygen (the signal at 4·3δ was a doublet of doublets) |
| 4·8 | 3 | |
| 6.2 | 4 | Olefinic proton, or aliphatic proton, shifted strongly, e.g. by R—CO—O— |
| 7.2, 7.6, 8.7 | | Pyridine residuals |
| 7.8 | | Aromatic proton (s) |
| 7·9 | | Total exchangeable protons (-OH, —COOH, water in sample and solvent) |

| Structure | Compound | Coupling H3–H4 | Coupling H4–H5 |
|---|---|---|---|
| I | 3-Galloylquinic acid | a-a | a-e |
| II | 5-Galloylquinic acid | a-a | a-e |
| III | 5-Galloylquinic acid (optical antipode) | e-e | e-a |

## CONCLUSIONS

The preparation of theogallin from an extract of unprocessed tea leaf was achieved by column partition chromatography; chromatographic and NMR analysis showed the product to be in a high state of purity.

The results of the present studies are entirely consistent with the structure tentatively predicted by Roberts and Myers,[4] of quinic acid monosubstituted at the 3-position with gallic acid.

## EXPERIMENTAL

### *Isolation of Theogallin*

Dried green tea leaf (300 g) was extracted with 80% MeOH (10 x 500 ml). The filtered extracts were combined and reduced to *ca. 600* ml at 40° under reduced pressure. This solution was washed repeatedly with $CHCl_3$, and residual organic solvent removed by evaporation. The aqueous phase was then extracted with EtOAc (5 x 500 ml). Traces of solvent were again removed from the aqueous phase by evaporation, and polyphenols precipitated by addition of an excess of sat. PbAc solution. The precipitate was suspended in MeOH and decomposed by $H_2S$. The filtrate was freeze-dried to a light-brown powder (5.8 g).

1 g of powder in the minimum $H_2O$, was applied to a column of cellulose (Whatman CC31; 70 x 2-8 cm) equilibrated with EtOAc saturated with $H_2O$ and eluted with the same solvent. Theogallin (identified from UV spectra and paper chromatographic data) was found as the only component in fractions (10 ml) 176-250 which were freeze-dried to a white powder (141 mg). The aqueous solution had $\lambda_{max}$ = 273 nm; $\Sigma_{max}$ = 6469 [cf. $\lambda_{max}$ = 276; $\Sigma_{max}$ = 10,450 (ref. 4)].

### *NMR Spectroscopy*

This was performed with a Varian HA-100D spectrometer, using TMS as an internal reference. Theogallin was dissolved in deuteropyridine; the clear amber solution obtained did not darken appreciably during the investigation.

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