Phytochemistry, Vol. 28, No. 8, pp. 2197–2199, 1989.
Printed in Great Britain.

0031–9422/89 \$3.00 + 0.00

SHORT REPORTS

4-HYDROXYUNDECYL DOCOSANOATE AND CYCLOARTENONE IN *ARTOCARPUS INTEGRA* LATEX

RADHA PANT and KSHAMA CHATURVEDI

Chemistry Department, Allahabad Agricultural Institute, Allahabad 211 007, India

(*Received* 5 *December* 1988)

Key Word Index—*Artocarpus integra*; Moraceae; cycloartenone; cycloartenyl acetate; artostenone; fatty acid ester.

Abstract—A hitherto unreported fatty acid ester occurring in the latex of *Artocarpus integra* is reported and its structure determined as 4-hydroxyundecyl docosanoate. Contrary to the earlier concept that cycloartenone occurred in the *Artocarpus integra* latex exclusively as its enol esters of its α-isomer, it has been obtained effortlessly by merely boiling the latex with ethanol without involving its hydrolysis.

INTRODUCTION

Nath and his collaborators [1–7] and Banerji and Bhattacharyya [8, 9] reported the occurrence of artostenone ($C_{30}H_{50}O$), an α,β-unsaturated steroidal ketone in the unsaponifiable fraction of the Jack fruit (*Artocarpus integra*) latex. Balakrishna and Seshadri [10–12] confirmed this work by obtaining the compound from the saponifiable fraction of the latex. However, Barton [13] subsequently proved the ketone to be a triterpenoid with molecular formula $C_{30}H_{48}O$ and not a steroid. He prepared several transformation products from this compound and named it cycloartenone. Employing both physical and chemical methods Barton [13] also demonstrated the presence of an isopropyledene group in a side chain and of a cyclopropane ring in the compound.

Recently *Artocarpus integra* latex, when boiled with ethanol was observed to yield large shining plates of a compound melting sharply at 109° in appreciable quantities. As no reference was traceable to the appearance of any compound from Jack fruit latex on merely boiling it with ethanol, it was considered worthwhile to re-examine the latex and to study the compounds obtained in detail.

RESULTS AND DISCUSSION

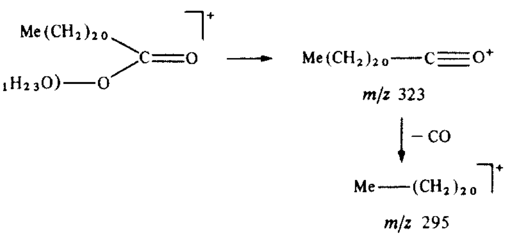
The yellow solid material obtained after filtering the hot ethanolic extract of the latex of *A. integra* was dissolved in *n*-hexane and applied to a silica gel column. Elution with the same solvent gave a number of compounds of which the first one was identified as cycloartenyl acetate.

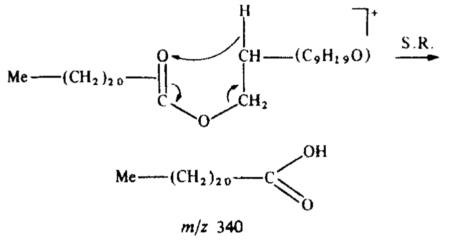
The next compound to be eluted was a white amorphous saturated compound, transparent under UV light, and melting at 76°. Elemental analysis and M_r $[M]^+$ m/z 510 gave $C_{33}H_{66}O_3$ as its molecular formula. (Found: C, 77.72%; H, 13.09%; $C_{33}H_{66}O_3$ requires C, 77.6%; H, 13.0%). The compound showed the absence of carbonyl or carboxyl groups nor did it respond to any test for terpenoids or steroids but appeared to be an ester as evidenced by the IR band at 1742 cm^{-1}. The absorption bands at 1470, 750 and 735 cm^{-1} were considered to be diagnostic [14–16] of the bending vibration of $(CH_2)_n$ (where *n* is more than four). The band at 3450 cm^{-1} assignable to a hydroxy group was confirmed by acetylation of the compound when a monoacetate was obtained. The IR bands of the acetate at 1742, 1700 and 1240 cm^{-1} with the conspicuous absence of the band at 3450 cm^{-1} exhibited by the parent compound indicated the presence of only one esterifiable hydroxy group. The band at 2960 cm^{-1} is suggestive of the stretching vibration of a methylene group.

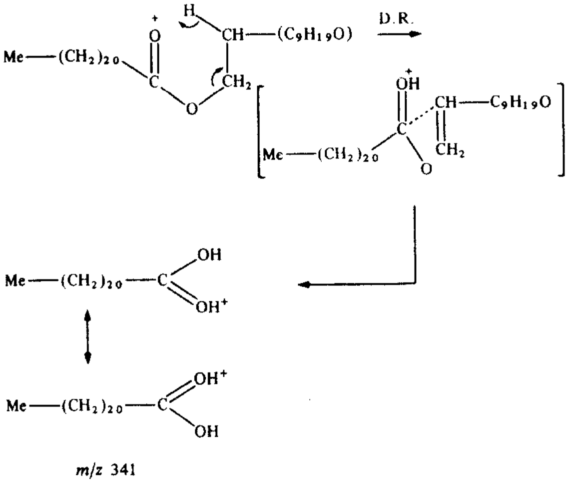
The signal at δ4.10 (*t*, 2H) in the ^1H NMR is assignable to a methylene ester and that at δ0.8 (6H) to the presence of two methyl groups. The triplet at δ2.30 (2H) indicated the location of the methylene groups as adjacent to the carbonyl group of the ester. While the multiplet at δ3.72 (1H) accounts for the attachment of the proton to the carbon linked to the hydroxy group, the singlet at δ1.26 (54H) showed the presence of 27 methylene groups. All the above evidence suggested the parent compound to be a saturated C_{33} aliphatic hydroxyl ester.

The exact nature and the size of the alkyl groups, position of the hydroxy group and the ester linkage were ascertained from the mass spectrum of the compound. It showed a $[M]^+$ at m/z 510. The $[M+1]^+$ (m/z 511) perhaps denoted the presence of a free -OH group [17] while the small one at m/z 492 could be the loss of one water molecule. The significant peaks at m/z 323 and 295 (base peak) point to the formation of $R{-}C{\equiv}O^+$ and R^+ ions as schematically represented below according to Dudley and Ian [18].

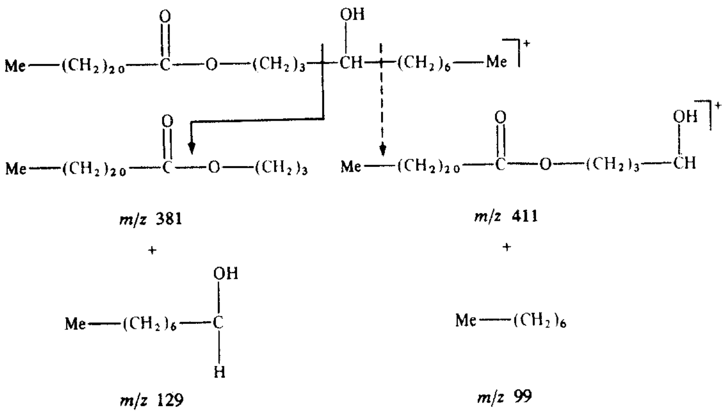
The peaks at m/z 340 and 341 explain the single and the double re-arrangements of hydrogen atoms resulting respectively in the formation of ionized and protonated carboxylic acids as shown below,



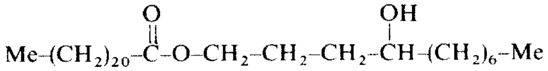




The peaks appearing at *m/z* 99 and 129 depict the presence of -OH group at C-4 as represented schematically below,



From the observations made above, the fatty acid ester isolated has been assigned tentatively the following structure,


$$Me\text{-}(CH_2)_{20}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{OH}{|}}{C}H\text{-}(CH_2)_6\text{-}Me$$

Another compound that eluted in a very small quantity (*ca* 200 mg), crystallized in rectangular shiny transparent plates and was characterized as cycloartenone. Interestingly, the major portion of this compound crystallized out in shining plates from the hot ethanolic extract of the latex on cooling.

EXPERIMENTAL

The white viscous sticky material that oozed out from the stem of freshly harvested fruits of *A. integra* Merr. was collected in shallow earthenware bowls and refrigerated for 3–4 hr. The serum-free gummy material (100 g) was extracted exhaustively with EtOH when a pale yellow oily liquid and a gummy material settled out. The latter was removed and discarded. The molten sticky material which solidified on cooling, was dissolved in *n*-hexane and subjected to CC.

The first compound to be eluted crystallized in white shining needles, mp 118–119°. Elemental analysis and M_r from MS as $[M]^+$ *m/z* 468 corresponded to the molecular formula $C_{32}H_{52}O_2$. (Found: C, 82.28%; H, 10.76%; $C_{32}H_{52}O_2$ requires C, 82.40%; H, 10.73%). The IR band at 1744 cm^{-1} showed the presence of an ester ($>$C=O group). ^{1}H NMR (CDCl$_3$, 90 MHz) recorded four methyl groups on saturated carbon atoms (δ, 0.83–0.97, 12H), two one proton multiplets of a cyclopropane ring (δ, 0.57, 0.36), two vinyl methyl groups (δ, 1.60, 1.69, 6H), a –C–Me group (δ, 2.08, 3H), a –CH–OAc group (δ, 4.56, 1H) and an olefinic proton (δ, 4.65, 1H). The above evidence suggested the compound to be cycloartenyl acetate. Identity was established by mmp, hydrolysis of the compound to cycloartenol, re-esterification to the original acetate and comparison with IR, NMR and MS of an authentic sample of cycloartenyl acetate.

The white amorphous compound (mp 76°) that was eluted next was identified as a fatty ester. The analytical data of this compound are detailed under Results and Discussion.

The hot EtOH extract of the latex was quickly filtered through glass wool into a beaker where it deposited large, shining transparent plates which on re-crystallization had mp 109° (yield, 0.9 g). The compound was identified as cycloartenone by comparison of its physical and chemical properties (IR, NMR, MS, mp, mmp and co-TLC) with those of an authentic specimen of cycloartenone. Interestingly, contrary to earlier reports [10–12] that cycloartenone occurred exclusively as enol esters of its α-isomer, it has now been obtained simply by boiling the latex of *A. integra* with EtOH without hydrolysing the latex.

Acknowledgement—The authors are grateful to Dr F. A. Hussaini, (The Central Drug Research Institute, Lucknow) for discussions and helpful suggestions.

REFERENCES

1. Nath, M. C. (1937) *Z. Physiol. Chem.* **247**, 9.
2. Nath, M. C. (1937) *Z. Physiol. Chem.* **249**, 71.
3. Nath, M. C. (1937) *Sci. Cult.* **3**, 297.
4. Nath, M. C. and Mukherjee, S. K. (1939) *J. Indian Chem. Soc.* **16**, 229.
5. Nath, M. C. and Sen Gupta (1939) *J. Indian Med. Res.* **27**, 171.
6. Nath, M. C. and Chakraborti, M. K. (1945) *J. Indian Chem. Soc.* **22**, 19.
7. Nath, M. C., Chowdhury, S. R. and Uddin, M. (1946) *J. Indian Chem. Soc.* **23**, 245.
8. Banerjee, K. and Bhattacharyya, J. (1938) *Sci. Cult.* **4**, 60.
9. Banerjee, K. and Bhattacharyya, J. (1939) *Z. Krist.* **100**, 420.
10. Balakrishna, K. J. and Seshadri, T. R. (1947) *Proc. Indian Acad. Sci.* **26A**, 46.
11. Balakrishna, K. J. and Seshadri, T. R. (1947) *Proc. Indian Acad. Sci.* **26A**, 203.
12. Balakrishna, K. J. and Seshadri, T. R. (1948) *Proc. Indian Acad. Sci.* **27A**, 409.
13. Barton, D. H. R. (1951) *J. Chem. Soc.* 1444.
14. Thompson, H. W. and Tortington, P. (1945) *Trans. Faraday Soc.* **41**, 246.
15. Khadem, H. E. and Rahman, M. M. A. (1965) *J. Chem. Soc.* 3488.
16. Bellamy, L. J. (1956) in *The Infrared Spectra of Complex Organic Molecules*, 2nd. Edn, p. 13. Wiley, New York.
17. Biemann, K., Gapp, F. and Seibl, J. (1959) *J. Am. Chem. Soc.* **81**, 2274.
18. Williams D. H. and Fleming, I. (1988) in *Spectroscopic Methods in Organic Chemistry*, 4th edn, pp. 169–170. McGraw–Hill, New Delhi.

Phytochemistry, Vol. 28, No. 8, pp. 2199–2201, 1989.
Printed in Great Britain.

0031–9422/89 $3.00+0.00
Pergamon Press plc.

8-EPIKINGISIDE AND ITS VANILLATE ESTER, ISOLATED FROM *GENTIANA PYRENAICA*

JULIAN GARCIA,* STEPHANE LAVAITTE† and CLAUDE GEY†

Laboratoire de Pharmacognosie, UFR de Pharmacie, Université Joseph Fourier-Grenoble I, Domaine de la Merci, F-38706 La Tronche Cedex, France; †CERMAV, BP 53 X, F-38041 Grenoble Cedex, France

(*Received in revised form* 5 *January* 1989)

Key Word Index—*Gentiana pyrenaica*; Gentianaceae; secoiridoid glucoside; 8-epikingiside; 6′-vanilloyl 8-epikingiside.

Abstract—8-Epikingiside and 6′-vanilloyl 8-epikingiside, a new natural compound, have been isolated from the aerial parts of *Gentiana pyrenaica*. The structures were elucidated on the basis of spectroscopic data.

INTRODUCTION

In a recent paper we reported the presence of two iridoid glucosides, loganin and 6′-(2*R*-methyl-3-veratroyloxy propanoyl) loganin, in the aerial parts of *Gentiana pyrenaica* L. (Gentianaceae) [1]. In the course of our investigation on the monoterpenic constituents of the title species we now describe the isolation and structure elucidation of the known 8-epikingiside (**1**) along with 6′-vanilloyl 8-epikingiside (**2**) a new natural secoiridoid glucoside.

RESULTS AND DISCUSSION

Aerial parts of *G. pyrenaica* were extracted as described in the experimental. Compounds **1** and **2** were obtained from the chloroform extract by centrifugal TLC and HPLC using ordinary silica gel and RP-18 columns, respectively.

The UV spectrum of compound **1** showed an intense absorption band at 237 nm characteristic of a conjugated carbonyl function. Furthermore, its ^{1}H NMR spectrum displayed a methoxycarbonyl singlet at $\delta 3.72$ and an olefinic doublet at 7.58 (H-3). These data, together with a positive vannillin reaction, suggested **1** to be a secoiridoid.

Acetylation of **1** with acetic anhydride–pyridine gave a tetraacetate (**1a**) which exhibited ^{1}H NMR resonances of

---

*Author to whom correspondence should be addressed.