

SHORT COMMUNICATION

TRITERPENES AND STEROLS OF COFFEE OIL

A. ALCAIDE, M. DEVYS and M. BARBIER

Institut de Chimie des Substances Naturelles,
C.N.R.S., 91-Gif sur Yvette, France

and

H. P. KAUFMANN and A. K. SEN GUPTA*

Bundesanstalt für Fettforschung, Münster, Germany

(Received 12 April 1970)

Abstract—Samples of triterpenes and sterols previously isolated from coffee oil and reported to contain lanosterol and coffeasterol have been reexamined by TLC and mass spectrometry. The presence of lanosterol is not confirmed; cycloartenol, cycloartanol and probably 24-methylenecycloartanol have been detected. The sterol fraction described as coffeasterol is a mixture of at least six methylsterols.

INTRODUCTION

In 1964, Kaufmann and Sen Gupta¹ analysed the unsaponifiable fraction of coffee oil. Three triterpenes were identified as lanosterol, dihydrolanosterol and squalene. A new C₃₁ sterol was also found, coffeasterol, for which the structure 4-ethylidene 8,24-stigmastadiene-3 β -ol was proposed. In 1968, Goad² repeated the analysis of the triterpene alcohols in coffee oil and failed to find lanosterol. As authentic lanosterol has been rarely found in higher plants, its presence in coffee beans would have been of some interest.

TLC and mass spectrometry permitted a reexamination of the original preparations isolated in 1964, but the presence of lanosterol could not be confirmed.

RESULTS

Triterpene Alcohols

The TLC of the acetates showed three substances with R_f s of cycloartanol acetate (or dihydrolanosterol acetate; *ca.* 10% R_f 0.65), cycloartenol acetate (or lanosterol acetate; *ca.* 60% R_f 0.45) and 24-methylenecycloartanol (or 24-methylene dihydrolanosterol; *ca.* 30% R_f 0.35). The three compounds were isolated by preparative TLC. The epoxide acetate of the main product (R_f 0.45) was prepared and compared by TLC with authentic epoxide acetates of lanosterol (diepoxide R_f 0.20) and of cycloartenol (monoepoxide R_f 0.40); it is thus identified as the epoxide of cycloartenol. Mass spectrometry of the acetate confirmed this result: molecular ion at m/e 468, 453 (M-15), 408 (M-60), 393 (M-60-15); a peak at m/e 286 is in agreement with the cyclopropane ring at 9-19.³ The acetate of R_f 0.35 possesses a molecular ion at 482 with main fragments at 467 (M-15), 422 (M-60), 407 (M-60-15); at m/e 300 is found a fragment corresponding to the presence of the cyclopropane ring at 9-19 and a side chain as in 24-methylenecycloartanol (the isomeric cyclolaudenol can not be

* Present address: Unilever Forschungslaboratorium, Hamburg, Germany.

¹ H. P. KAUFMANN and A. K. SEN GUPTA, *Fette Seifen Anstrichmittel* **66**, 461 (1964).

² L. J. GOAD, unpublished results cited by G. PONSINET and G. OURISSON, *Phytochem.* **7**, 762 (1968).

³ H. E. AUDIER, R. BEUGELMANS and B. C. DAS, *Tetrahedron Letters* 4341 (1966).

excluded). Too little of the product with R_f 0.65 was obtained for further study; but after epoxidation the acetate had an unchanged R_f ; this result and the R_f could fit cycloartanol.

Coffeasterol

TLC on $\text{SiO}_2\text{-AgNO}_3$ showed two fractions of R_f 0.35 and 0.40 which were isolated and analysed by mass spectrometry. The substance of R_f 0.35 has a molecular ion at m/e 412 and probably a methylene group at C-24 as the "cyclic" elimination process of the side chain³ is observed with an ion at 328. The ion corresponding to the total elimination of the side chain is at 285 ($\text{M-C}_9\text{H}_{17}$ and transfer of 2H) and the fragmentation through cycle D leads to m/e 227. There are small peaks at M-18 and at M-15-18 in agreement with the lack of unsaturation in position 5. By deduction, the cyclic part of the molecule bears an extra methyl group, probably in position 4. From the nature of the different substitutions, the product could be 24-methylenelophenol or an isomer. The substance of R_f 0.40 is still a mixture of homologous series with molecular ions at m/e 428, 426, 414 and 400, the most abundant being at 426. The main component has a C_{10} side chain probably with an ethylidene group at C-24; ("cyclic" elimination of the side chain). This compound could be ethylidene-24-lophenol, and the minor homologues, with side chains in C_8H_{17} (m/e 400), C_9H_{19} (m/e 414), C_9H_{17} (m/e 412) and $\text{C}_{10}\text{H}_{21}$ (m/e 428) could consist of a biosynthetic series belonging to the lophenol family.

EXPERIMENTAL

The triterpene alcohols and the coffeasterol fractions re-investigated are those previously isolated by Kaufmann and Sen Gupta.¹ The acetates of the triterpene alcohols were separated by TLC on AgNO_3 -impregnated alumina using hexane EtOAc (20:1). The coffeasterol fraction was chromatographed on $\text{SiO}_2\text{-AgNO}_3$ TLC with pentane-EtOAc-acetone (18:4:1). The epoxide acetates were prepared according to Ourisson *et al.*⁴ and separated on $\text{Al}_2\text{O}_3\text{-AgNO}_3$ with hexane-EtOAc (20:1). Mass spectrometric determinations were made on an Atlas CH₄ and an AEI MS9.*

Acknowledgement—Thanks are due to Professor E. Lederer for his interest.

* Mass spectrometric determinations were performed by MM. Cosson and Varenne under the direction of Dr. B. C. Das.

⁴ G. PONSINET and G. OURISSON, *Phytochem.* **4**, 799 (1965).