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THE TRITERPENES OF COMMIPHORA IV (1)
MASS SPECTRA AND ORGANIC ANALYSIS V (2)
MASS SPECTROSCOPIC STUDIES AND THE STRUCTURE OF COMMIC ACIDS A AND B

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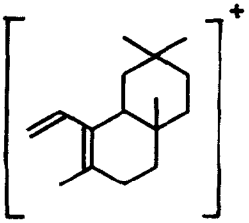
The isolation from Commiphora pyracanthoides Engl. of triterpene acids (3) and the structure of three of these (commic acids C and D (4) and commic acid E (1)) have been described. On the basis of IR spectral studies, some doubt has since been tacitly expressed (5) about the structure of commic acid C, and the present note is intended to bring support for our previous structures and to suggest reasonable structures for acids A and B.

The mass spectra (6) of methyl commates A to E are illustrated in FIG. 1-5. It is clear from the important fragment at m/e 218, arising from a retro-Diels-Alder fission of ring C (7), that there is no oxygen function in rings C, D or E. The most marked difference between esters C and D is in the relative intensities of the fragments at m/e 218 and 203, the latter being 50% of the former in the case of ester D, and 75% in the case of ester C. This relative difference in intensities is repeated in two other derivatives of esters C and D that we have examined (as shown in TABLE 1) and especially in norolean-12-ene (FIG. 6) and norurs-12-ene (FIG. 7)

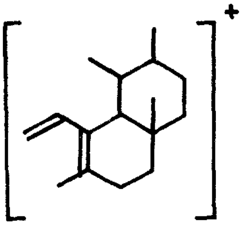
TABLE 1.

Substance	Reference	Intensity 203 as % 218
Methyl commate C	3	75
Diosphenol C	4	85
Norolean-12-ene	4	60
Methyl commate D	4	53
Diosphenol D	4	39
Norurs-12-ene	7	33

The easier loss of a methyl group from the fragment at m/e 218 in the C series is understandable if these compounds are derived from oleanane and the D series from ursane, the latter giving an ion at m/e 218 with only one quaternary methyl group :



m/e 218 in Series C

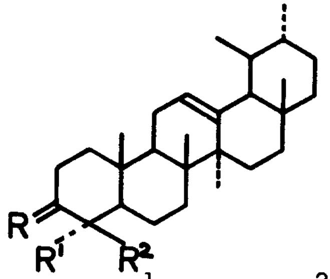


Series D

The rest of the molecule is obviously very similar, and in view of the allocation of structure to methyl commate D, we have little doubt that our views concerning the structure of methyl commate C are correct.

The mass spectrum of methyl commate B shows the fragment at m/e 203 to be 54% of that at m/e 218. This is near the value for methyl commate D, but lower than that for methyl commate C, so we prefer an ursane structure for acid B.

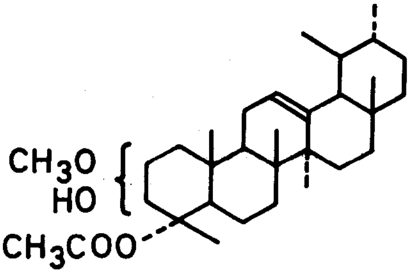
It was found that commol B (3) forms an acetonide in the same way as commol C and commol D (4), and, although we were unable to crystallize this, it showed no hydroxyl or carbonyl bands in the IR. The hydroxyl and carboxyl groups in commic acid B are therefore 1,2- or 1,3-, and it seems likely that it is a 3-hydroxyurs-12-en-23 (or 24)-oic acid. Oxidation of methyl commate B with chromic oxide in pyridine yielded a ketone (I), m.p. 208-210° with two strong carbonyl bands in the IR spectrum (in CH_2Cl_2) at 1472 and 1711 cm^{-1}, which are very close to the values quoted (8) for methyl-β-boswellonate (II). Both the 3α- and 3β-hydroxy-esters corresponding to the latter ketone are known (8), but neither of these is identical with methyl commate B, for which we prefer the structure methyl 3β-hydroxyurs-12-en-23-oate (III).



I $R = O$, $R^1 = COOCH_3$, $R^2 = H$

II $R = O$, $R^1 = H$, $R^2 = COOCH_3$

III $R = H, OH$ (β), $R^1 = COOCH_3$, $R^2 = H$



IV

We are no longer sure that methyl commate A is an artefact (see ref. 3), since we were unable to effect any methylation of methyl commates C or D with diazomethane even in the presence of HBF_4 (9), and it seems more likely that commic acid A is a genuine constituent of Commiphora pyracanthoides. Only very small amounts of the ester were available, but the similarity of its mass spectrum with the other esters would indicate a 3-oxyurs-12-en-23 (or 24)-oic acid derivative. The loss of methanol from the parent ion rather than water (fragment at m/e 468 but not at m/e 482) confirms the presence of a methyl ether, but we do not feel that this evidence alone is sufficient to place it unquestionably at C-3 (10). We therefore prefer to leave the structure as IV.

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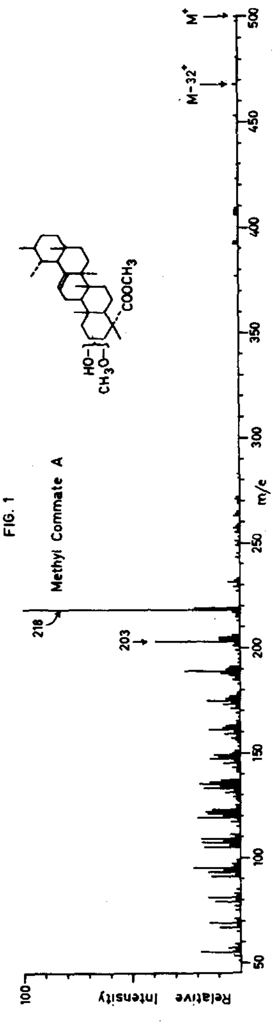

FIG. 1

Methyl Commate A

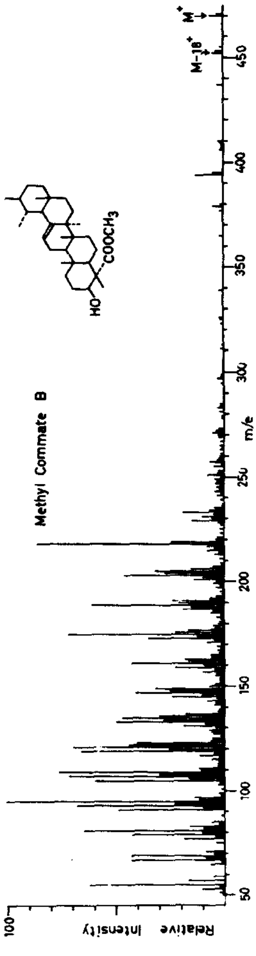

FIG. 2

Methyl Commate B

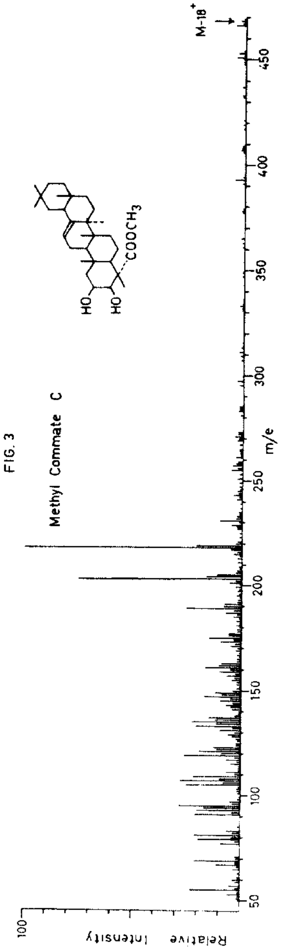

FIG. 3

Methyl Commate C

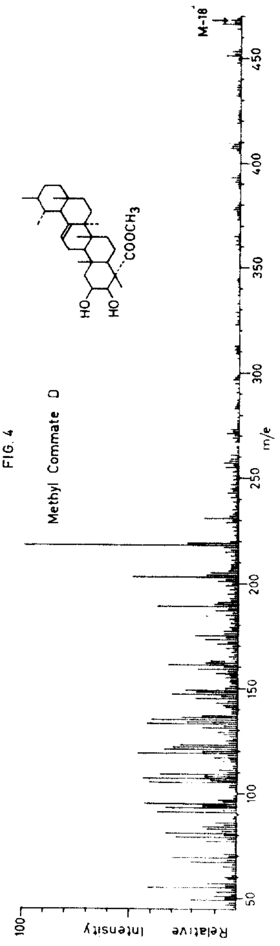

FIG. 4

Methyl Commate D

FIG. 5

Methyl Commate E

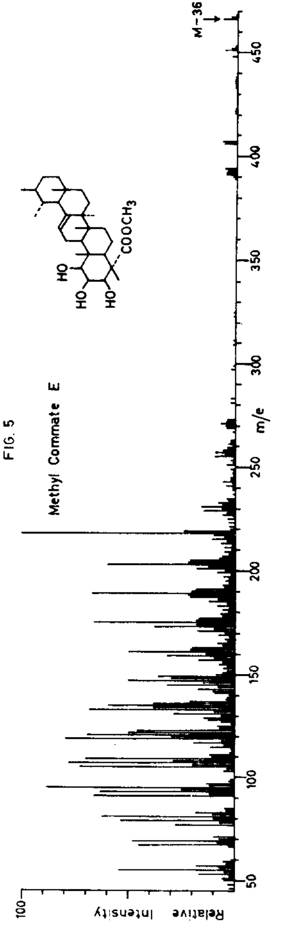

FIG. 6

Norolean-12-ene

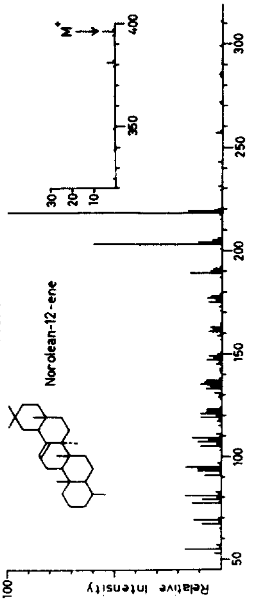

FIG. 7

Norurs-12-ene